Supplementary material (ESI) for Chemical Communications


# Synthesis and characterization of thiochromone *S,S*-dioxides as new photolabile protecting groups.

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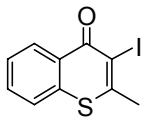
## Supplementary Information

**General**: All reactions were conducted in oven-dried (135 $^{o}$C) glassware under an inert atmosphere of dry nitrogen. The progress of reactions were monitored by silica gel thin layer chromatography (tlc) plates (mesh size 60Å, MERCK), visualized under UV and charred using phosphomolybdic acid/sulfuric acid. Products were purified by flash column chromatography (FCC) on 40-63 μm silica gel 60 (MERCK). Proton nuclear magnetic resonance spectra ($^{1}$H NMR) were recorded on JEOL JNM-ECP 500 (500 MHz). Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. Data is reported as follows: chemical shift, integration, coupling constants (Hz), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, sept=septet, br=broad, m=multiplet). Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) were recorded on a JEOL JNM-ECP 500 instrument (125 MHz). Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard or the middle peak of chloroform-*d*(77.0 ppm). Compound **3** was prepared according to the literature procedure.[6]

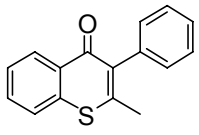
### 3-Iodo-2-methyl-4H-thiochromen-4-one (4)[7]




A mixture of 2-methyl-4H-thiochromen-4-one (**3**) (1.0 mmol, 176 mg), $I_2$ (1.2 mmol, 305 mg) and CAN (1.1 mmol, 603 mg) in dry MeCN (4.0 ml) was stirred at 60 $^{o}$C under $N_2$. The reaction was continued until the substrate disappeared (determined by TLC). Then the mixture was poured into a cold sat. $Na_2S_2O_3$ aq. and extracted with $CH_2Cl_2$. The combined organic layer was washed with $H_2O$, dried over anhydrous $MgSO_4$ and evaporated. Flash chromatography of the residue over silica gel gave to **4** (0.79 mmol,

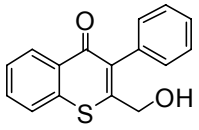
238 mg, 79%) as yellow solids.
$^1$H-NMR ($CDCl_3$/TMS) δ: 8.52 (1H, *J* = 7.9 Hz, d), 7.60 (1H, *J* = 7.6, 7.9 Hz, dd), 7.55-7.51 (2H, m), 2.62 (3H, s). $^{13}$C-NMR ($CDCl_3$) δ: 175.46, 151.12, 136.32, 131.59, 129.77, 128.12, 126.90, 124.86, 103.70, 32.44.

**2-Methyl-3-phenyl-4H-thiochromen-4-one (5)**




To a dry flask containing 3-iodo-2-methyl-4H-thiochromen-4-one (**4**) (1.0 mmol, 302 mg), $Pd(PPh_3)_2Cl_2$ (0.03 mmol, 21 mg), $PhB(OH)_2$ (1.3 mmol, 159 mg), and $K_2CO_3$ (4.0 mmol, 552 mg) were added DMF (3.2 ml) and $H_2O$ (0.8 ml). After stirring of the reaction mixture for 4 h, the aqueous layer was extracted with AcOEt. The combined organic extract was washed with water and brine, and then dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **5** (0.93 mmol, 237 mg, 93%) as white solids.
$^1$H-NMR ($CDCl_3$/TMS) δ: 8.51 (1H, *J* = 8.6 Hz, d), 7.61-7.59 (2H, m), 7.53-7.49 (1H, m), 7.45 (2H, *J* = 7.6, 7.6 Hz, dd), 7.37 (1H, *J* = 7.6, 7.6 Hz, dd), 7.21 (2H, *J* = 7.6 Hz, d), 2.26 (3H, s). $^{13}$C-NMR ($CDCl_3$) δ: 179.14, 147.18, 136.63, 136.40, 136.00, 131.16, 131.09, 129.77, 129.38, 128.45, 127.55, 127.35, 125.52, 22.52.

**2-(Hydroxymethyl)-3-phenyl-4H-thiochromen-4-one (1)**

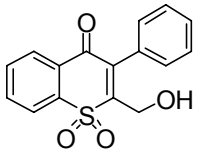



To a dry flask containing 2-methyl-3-phenyl-4H-thiochromen-4-one (**5**) (1.0 mmol, 252 mg) and $SeO_2$ (1.2 mmol, 133 mg) was added chlorobenzene (5.0ml). The solution was refluxed for 12 h. After addition of sat. $NaHCO_3$ aq., the aqueous layer was extracted with $CH_2Cl_2$ and the combined organic extract was dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue filtered through a pad of silica gel using 1 : 1 hexane-AcOEt to give aldehyde. $NaBH_4$ was put into a flask, and then the obtained

aldehyde and dry MeOH were added. The solution was stirred at 0°C for 1 h, and diluted with sat. $NH_4Cl$ aq. (5.0 ml). The aqueous layer was extracted with $CH_2Cl_2$. The combined organic extract was washed with water and brine, and then dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel. Recrystallization from hexane/AcOEt solution gave **1** (0.38 mmol, 104 mg, 38 %) as white solids.

$^1$H-NMR ($CDCl_3$/TMS) δ: 8.51 (1H, *J* = 7.9 Hz, d), 7.67 (1H, *J* = 7.9 Hz, d), 7.64-7.61 (1H, m), 7.53 (1H, *J* = 7.9, 7.9 Hz, dd), 7.44 (2H, *J* = 7.3, 7.3 Hz, dd), 7.38 (1H, *J* = 7.3 Hz, t), 7.19 (2H, *J* = 7.3 Hz, d), 4.54 (2H, s). $^{13}$C-NMR ($CDCl_3$) δ: 179.29, 152.34, 136.85, 135.30, 134.65, 131.32, 131.13, 129.43, 129.26, 128.74, 128.07, 127.62, 126.63, 63.49. IR ($CHCl_3$) 1619, 1591, 1498, 1342, 1220, 1208, 1083, 790, 776, 733, 729, 700, 599.
HRMS(EI) calcd for $C_{16}H_{12}O_2S$ 268.0558; found: 268.0554.

**2-(Hydroxymethyl)-3-phenyl-4H-sulfonylchromen-4-one (2)**




To a dry flask containing 2-(hydroxymethyl)-3-phenyl-4H-thiochromen-4-one (**1**) (1.0 mmol, 252 mg) and *m*-CPBA (70 %) (2.1 mmol, 515 mg) was added $CH_2Cl_2$ (2.0 ml). The solution was stirred at room temperature for 8 h. The mixture was diluted with sat. $Na_2S_2O_3$ aq. (3.0 ml) and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic extract was washed with sat. $NaHCO_3$ aq. and brine, and then dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **2** (0.85 mmol, 255 mg, 85 %) as yellow solids.

$^1$H-NMR ($CDCl_3$/TMS) δ: 8.21 (1H, *J* = 7.9 Hz, d), 8.10 (1H, *J* = 7.9, d), 7.89 (1H, *J* = 7.9 Hz, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9 Hz, 7.9 Hz, dd), 7.50-7.46 (3H, m), 7.38-7.34 (2H, m), 4.62(2H, s). $^{13}$C-NMR ($CDCl_3$) δ: 178.60, 147.79, 142.67, 140.02, 134.62, 133.38, 130.62, 129.61, 129.42, 129.13, 129.03, 128.36, 123.06, 56.97. IR ($CHCl_3$) 1720, 1665, 1587, 1574, 1442, 1303, 1217, 1156, 1131, 1065, 1030, 846, 803, 743, 699, 674, 599, 544.

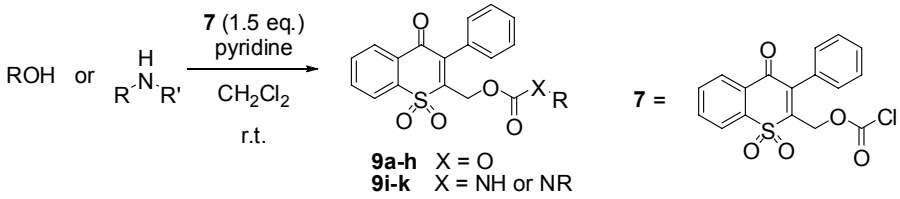
HRMS(EI) calcd for $C_{16}H_{12}O_2S$ 300.0456; found: 300.0457.

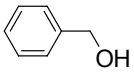
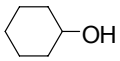
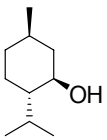
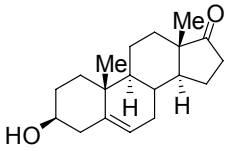
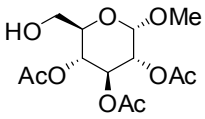
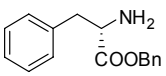
**General procedure for the synthesis of carbonate derivatives 9.**

Compound **1** or **2** (1.5 mmol) and aliquat®336 (10 mg) were dissolved in THF (1.0 ml) and toluene (1.0 ml). phosgene gas was generated by using Cartridge for Phosgene Generation (Aldrich Inc.) at 80 $^oC$ and was introduced at 0 $^oC$. The solution was stirred at room temperature for 24 h. $N_2$ gas was bubbled for 5min to remove phosgene gas in the flask. The residue filtered through a pad of silica gel using 1 : 1 hexane-AcOEt to give **6** or **7**.

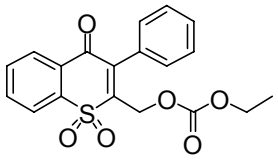
Chloroformate derivative **6** or **7** (1.5 mmol) dissolved in $CH_2Cl_2$ (1.0 ml) was added dropwise to a mixture of corresponding alcohol (1.0 mmol) or amine (1.0 mmol) and pyridine (1.0 ml) at 0 $^oC$. After stirring of the reaction mixture for appropriate time at room temperature, $H_2O$ (10 ml) was added. The aqueous layer was extracted with $CH_2Cl_2$, and the combined extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **9** (see ESI-Table 1).

ESI-Table 1 Protection yield of alcohols and amines.



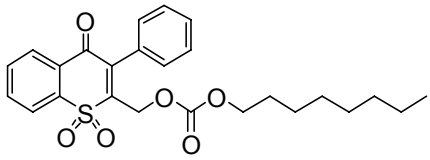

| Entry | Substrate | Alcohol or Amine | Time(h) | Protection yield (%) |
|---|---|---|---|---|
| 1 | **9a** | EtOH | 3.0 | 98 |
| 2 | **9b** | $C_8H_{17}OH$ | 3.0 | 91 |
| 3 | **9c** |  | 3.0 | 84 |
| 4 | **9d** |  | 8.0 | 67 |
| 5 | **9e** |  | 8.0 | 68 |
| 6 | **9f** |  | 8.0 | 71 |
| 7 | **9g** |  | 8.0 | 66 |
| 8 | **9h** |  | 3.0 | 88 |
| 9 | **9i** | $C_4H_9NH_2$ | 1.0 | 96 |
| 10 | **9j** | $Et_2NH$ | 1.0 | 91 |
| 11 | **9k** |  | 1.0 | 90 |

**9a**



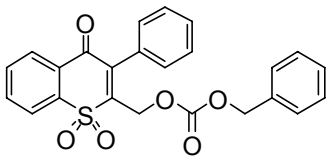
Yield 98 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.12 (1H, *J* = 7.9 Hz, d), 8.04 (1H, *J* = 7.9 Hz, d,), 7.83 (1H, *J* = 7.9, 7.9 Hz, dd), 7.71 (1H, *J* = 7.9, 7.9 Hz, dd), 7.42-7.41 (3H, m), 7.23-7.19 (2H, m), 5.03 (2H, s), 4.14 (2H, q, *J* = 7.1 Hz), 1.24 (3H, t, *J* = 7.0 Hz). $^{13}$C-NMR ($CDCl_3$) δ: 178.45, 154.10, 144.77, 144.12, 140.53, 134.77, 133.26, 130.67, 129.74, 129.07, 128.94, 128.92, 128.48, 123.19, 64.87, 60.52, 14.18. IR ($CHCl_3$) 1798, 1751, 1669, 1589, 1465, 1378, 1314, 1285, 1222, 1209, 1164, 1140, 1095, 997, 919, 791, 759, 727, 650, 542.
HRMS(FAB) calcd for $C_{19}H_{16}O_6S(M+Na)^+$ 495.0565; found: 495.0571.

**9b**



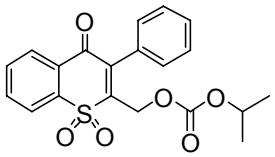
Yield 91 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.18 (1H, *J* = 7.9 Hz, d), 8.11 (1H, *J* = 7.9 Hz, d), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.50-7.46 (3H, m), 7.31-7.25 (2H, m), 5.10 (2H, s), 4.14 (2H, *J* = 7.0 Hz, t), 1.68-1.63 (2H, m), 1.35-1.27 (10H, m), 0.88 (3H, *J* = 7.0 Hz, t). $^{13}$C-NMR($CDCl_3$) δ: 178.49, 154.27, 144.79 ,144.20, 140.58, 134.80, 133.28, 130.71, 120.65, 129.77, 129.11, 128.98, 128.95, 128.50, 123.24, 69.08, 31.75, 29.13, 28.55, 25.57, 22.62, 14.09. IR ($CHCl_3$) 2958, 2929, 2852, 1756, 1669, 1589, 1493, 1466, 1463, 1397, 1362, 1335, 1256, 1223, 1231, 1208, 1163, 1140, 1123, 1071, 1030, 949, 850, 790, 778, 770, 759, 743, 735, 727, 725, 699.
HRMS(FAB) calcd for $C_{25}H_{28}O_6S(M^+ + Na)$ 479.1507; found: 479.1502.

**9c**



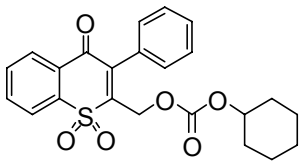
Yield 84 %, yellow solid. $^{1}$H -NMR ($CDCl_3$/TMS) δ: 8.19 (1H, *J* = 7.9 Hz, d), 8.12 (1H, *J* = 7.9 Hz, d), 7.90 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.48-7.43 (3H, m), 7.37-7.34 (4H, m), 7.27-7.26 (3H, m), 5.17 (2H, s), 5.11 (2H, s). $^{13}$C -NMR ($CDCl_3$) δ: 178.48, 154.10, 145.00, 144.00, 140.53, 134.81, 133.31, 130.64, 129.79, 129.09, 128.97, 128.63, 128.58, 128.53, 128.50, 128.36, 126.99, 123.26, 70.33, 60.67. IR ($CHCl_3$) 2546, 2253, 1794, 1752, 1669, 1465, 1382, 1315, 1267, 1223, 1208, 1164, 1127, 1096, 903, 792, 781, 728, 716, 650, 620.
HRMS(FAB) calcd for $C_{24}H_{18}O_6S(M^+ + Na)$ 457.0724; found: 457.0719.

**9d**



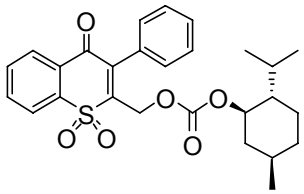
Yield 67 %, yellow solid. $^{1}$H -NMR ($CDCl_3$/TMS) δ: 8.18 (1H, d, *J* = 7.9 Hz), 8.11 (1H, d, *J* = 7.9 Hz), 7.89 (1H, dd, *J* = 7.9, 7.9 Hz), 7.78 (1H, dd, *J* = 7.9, 7.9 Hz), 7.50-7.47 (3H, m), 7.30-7.29 (2H, m), 5.09 (2H, s), 4.88 (1H, sept, *J* = 6.1 Hz), 1.30 (6H, d, *J* = 6.1 Hz). $^{13}$C-NMR ($CDCl_3$) δ: 178.46, 153.62, 144.65, 144.29, 140.57, 134.76, 133.24, 130.70, 129.70, 129.07, 128.93, 128.90, 128.45, 123.20, 73.11, 60.27, 21.67. IR ($CHCl_3$) 1744, 1663, 1589, 1467, 1443, 1373, 1365, 1267, 1223, 1210, 1208, 1163, 1141, 1123, 1092, 942, 910, 853, 833, 799, 774, 757, 744, 739, 727, 699, 669.
HRMS(FAB) calcd for $C_{20}H_{18}O_6S(M^+ + Na)$ 409.0724; found: 409.0722.

**9e**



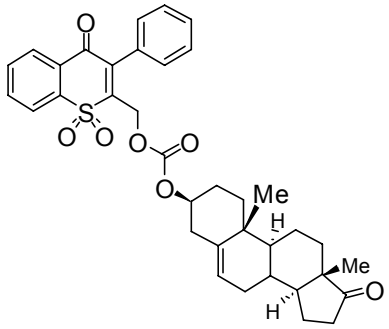
Yield 68 %, yellow solid. $^{1}$H -NMR ($CDCl_3$/TMS) δ: 8.19 (1H, *J* = 7.9 Hz, d), 8.12 (1H, *J* = 7.9 Hz, d), 7.90 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.49-7.47 (3H, m), 7.31-7.30 (2H, m), 5.09 (2H, s), 4.62-4.60 (1H, m), 1.91-1.89 (2H, m), 1.75-1.73 (2H, m), 1.58-1.50 (3H, m), 1.33-1.28 (3H, m). $^{13}$C-NMR ($CDCl_3$) δ: 178.48, 153.67, 144.62, 144.38, 140.61, 134.78, 133.26, 130.75, 129.73, 129.10, 128.94, 128.92, 128.49, 123.23, 77.89, 60.34, 31.42, 25.15, 23.60. IR ($CHCl_3$) 1745, 1669, 1583, 1444, 1332, 1315, 1272, 1256, 1222, 1208, 1165, 1140, 1126, 1070, 1033, 1005, 981, 850, 789, 781, 757, 747, 727, 699, 669.
HRMS(FAB) calcd for $C_{23}H_{22}O_6S$ ($M^+$ +Na) 449.1035; found: 449.1026.

**9f**



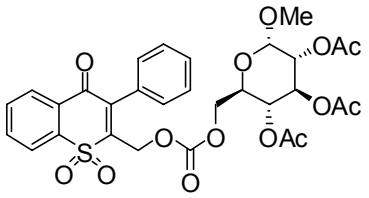
Yield 71 %, yellow solid. $^{1}$H -NMR ($CDCl_3$/TMS) δ: 8.18 (1H, *J* = 7.9 Hz, d), 8.11 (1H, *J* = 7.9 Hz, d), 7.88 (1H, *J* = 7.9, 7.9 Hz, dd), 7.77 (1H, *J* = 7.9, 7.9 Hz, dd), 7.47-7.45 (3H, m), 7.30-7.30 (2H, m), 5.12 (1H, *J* = 12.8 Hz, d), 5.04 (1H, *J* = 12.8 Hz, d), 4.51 (1H, *J* = 11.0, 4.3 Hz, td), 2.07-2.05 (1H, m), 1.97-1.96 (1H, m), 1.68-1.66 (2H, m), 1.44-1.42 (3H, m), 1.09-1.00 (2H, m), 0.92-0.88 (6H, m), 0.78 (3H, *J* = 6.7 Hz, d). $^{13}$C-NMR ($CDCl_3$) δ: 178.43, 153.81, 144.60, 144.31, 140.56, 134.70, 133.17, 130.71, 129.64, 129.03, 128.89, 128.83, 128.39, 123.19, 79.46, 60.25, 46.77, 40.44, 33.97, 31.31, 25.88, 23.23, 21.88, 20.62, 16.19. IR ($CHCl_3$) 1745, 1668, 1589, 1444, 1372, 1314, 1265, 1222, 1212, 1208, 1163, 1140, 1071, 951, 913, 847, 787, 785, 781, 779, 777, 775, 769, 767, 763, 758, 747, 738, 731, 699.
HRMS(ESI) calcd for $C_{27}H_{30}O_6S$ $(M-H)^-$ 481.1684; found: 481.1685.

**9g**



Yield 66 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.07 (1H, *J* = 7.9 Hz, d), 8.00 (1H, *J* = 7.9 Hz, d), 7.79 (1H, *J* = 7.9, 7.9 Hz, dd), 7.68 (1H, *J* = 7.9, 7.9 Hz, dd), 7.39-7.38 (3H, m), 7.22-7.20 (2H, m), 5.33 (1H, *J* = 4.9 Hz, d), 5.00 (2H, s), 4.42-4.36 (1H, m), 2.39-2.28 (3H, m), 2.03-1.95 (2H, m), 1.85-1.76 (4H, m), 1.61-1.55 (4H, m), 1.49-1.35 (2H, m), 1.20-1.18 (2H, m), 1.05-1.02 (1H, m), 0.94 (3H, s), 0.93-0.88 (1H, m), 0.79 (3H, s). $^{13}$C-NMR ($CDCl_3$) δ: 220.66, 178.22, 153.31, 144.39, 144.04, 140.36, 139.27, 134.63, 133.11, 130.57, 129.51, 128.93, 128.71, 128.69, 128.27, 122.96, 122.07, 78.37, 60.30, 51.43, 49.84, 47.27, 37.61, 36.53, 36.44, 35.60, 31.20, 31.18, 30.54, 27.29, 21.65, 20.11, 19.09, 13.34. IR ($CHCl_3$) 1736, 1669, 1589, 1467, 1443, 1375, 1314, 1267, 1252, 1221, 1219, 1210, 1164, 1140, 1070, 1020, 970, 943, 906, 850, 788, 769, 757, 751, 741, 732, 727, 669.
HRMS(ESI) calcd for $C_{36}H_{38}O_7S$ $(M-H)^-$ 613.2259; found: 613.2260.

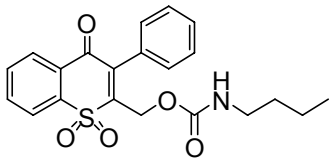
**9h**



Yield 88 %, yellow solid. $^{1}$H -NMR ($CDCl_3$/TMS) δ: 8.18 (1H, *J* = 7.9 Hz, d), 8.07 (1H, *J* = 7.9 Hz, d), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.50-7.49 (3H, m), 7.29-7.28 (3H, m), 5.56 (1H, *J* = 9.8, 9.8 Hz, dd), 5.20 (1H, *J* = 12.8 Hz, d), 5.05 (1H, *J* = 12.8 Hz, d), 4.98-4.93 (2H, m), 4.88 (1H, *J* = 10.4, 3.7 Hz, dd), 4.29 (1H, *J* = 12.5, 4.6 Hz, dd), 4.19 (1H, *J* = 12.2, 2.4 Hz, dd), 4.04-4.01 (1H, m), 3.40 (3H, s),

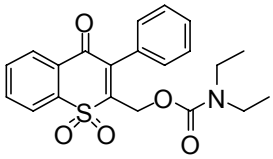
2.09 (3H, s), 2.07 (3H, s), 2.02 (3H, s). $^{13}$C-NMR ($CDCl_3$) 178.35, 170.58, 170.15, 169.89, 153.31, 144.72, 143.54, 140.53, 134.78, 133.26, 130.51, 129.81, 129.16, 128.94, 128.91, 128.53, 123.13, 96.71, 73.15, 70.90, 69.39, 66.74, 61.84, 61.37, 55.46, 20.73, 20.70, 20.68. IR ($CHCl_3$) 1756, 1669, 1463, 1371, 1316, 1268, 1237, 1223, 1208, 1166, 1140, 1096, 1070, 1034, 902, 792, 769, 756, 742, 719, 669.
HRMS(FAB) calcd for $C_{30}H_{30}O_{14}S$ ($M^+$+Na) 669.1254; found: 669.1245.

**9i**



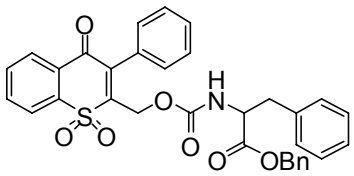
Yield 96 %, $^1$H -NMR ($CDCl_3$) δ: 8.18 (1H, *J* = 7.9 Hz, d,), 8.11 (1H, *J* = 7.9 Hz, d,), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.77 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.47-7.43 (3H, m), 7.28-7.26 (2H, m), 5.06 (2H, s), 4.82 (1H, s), 3.17 (2H, *J* = 7.3, 6.7 Hz, dd,), 1.51-1.44 (2H, m), 1.38-1.29 (2H, m), 0.91(3H, t, *J* = 7.3 Hz). $^{13}$C -NMR ($CDCl_3$) δ: 178.63, 154.96, 145.66, 143.82, 140.89, 134.68, 133.18, 131.04, 129.64, 129.10, 129.04, 128.88, 128.48, 123.11, 58.71, 40.99, 31.84, 19.82, 13.70.
IR ($CHCl_3$) 1732, 1669, 1589, 1516, 1428, 1312, 1224, 1161, 1077, 699, 600, 535
HRMS(FAB) calcd for $C_{21}H_{21}NO_5S$($M^+$+Na) 422.1038; found: 422.1042

**9j**



Yield 91 %, $^1$H -NMR ($CDCl_3$) δ: 8.18 (1H, *J* = 7.9 Hz, d,), 8.11 (1H, *J* = 7.9 Hz, d,), 7.88 (1H, *J* = 7.9, 7.9Hz, dd,), 7.76 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.48-7.44 (3H, m), 7.30-7.25 (2H, m), 5.07 (2H, s), 3.34-3.25 (4H, m), 1.19-1.10 (6H, m). $^{13}$C -NMR ($CDCl_3$) δ: 178.59, 154.44, 146.00, 143.48, 141.11, 134.62, 133.06, 131.12, 129.58, 129.04, 128.98, 128.81, 128.47, 123.04, 59.24, 41.99, 41.36, 13.93, 13.31.
IR ($CHCl_3$) 1738, 1701, 1669, 1590, 1476, 1428, 1381, 1313, 1271, 1169, 1077, 906, 856, 541, 524.
HRMS(FAB) calcd for $C_{21}H_{21}NO_5S$($M^+$+Na) 422.1038; found: 422.1036

**9k**

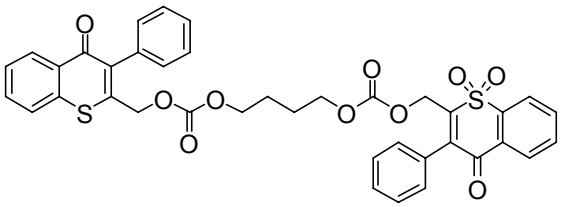



Yield 90 %, $^{1}$H -NMR ($CDCl_3$) δ: 8.15 (1H, *J* = 7.3 Hz, d), 8.08 (1H, *J* = 7.3 Hz, d), 7.84 (1H, *J* = 7.9, 7.9Hz, dd), 7.72 (1H, *J* = 7.9, 7.9Hz, dd), 7.44-7.39 (3H, m), 7.35-7.30 (3H, m), 7.28-7.17 (7H, m), 7.06-7.01 (2H, m), 5.46 (1H, *J* = 7.9Hz, d), 5.11 (3H, m), 4.97 (1H, *J* = 12.8Hz, d), 4.70-4.62 (1H, m), 3.08 (2H, *J* = 5.5Hz, d). $^{13}$C -NMR ($CDCl_3$) δ: 178.46, 170.77, 154.04, 144.96, 144.13, 140.59, 135.29, 134.89, 134.60, 133.08, 130.80, 129.52, 129.30, 128.96, 128.90, 128.74, 128.48, 128.46, 128.40, 128.32, 126.97, 123.01, 67.13, 58.53, 54.89, 38.06. IR ($CHCl_3$) 1731, 1668, 1589, 1507, 1443, 1389, 1313, 1233, 1223, 1208, 1162, 1139, 1078, 853, 699, 666, 543, 524.
HRMS(FAB) calcd for $C_{33}H_{27}NO_7S$($M^+$+Na) 604.1406; found:604.1399

Synthesis of **11**.

Chloroformate derivative **7** (0.2 mmol, 72 mg) dissolved in $CH_2Cl_2$ was added dropwise to a mixture of 1,4-butanediol (2.0 mmol, 180 mg) and pyridine (2.0 ml) at 0 $^{o}$C. After stirring of the reaction mixture for 3.0 h at room temperature, $H_2O$ (5.0 ml) was added. The aqueous layer was extracted with $CH_2Cl_2$, and the combined extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **13** (0.12 mmol, 46 mg, 58 %) as yellow solids. Chloroformate derivative **6** (0.5 mmol, 165 mg) dissolved in $CH_2Cl_2$ was added dropwise to a mixture of **13** (0.1 mmol, 40 mg) and pyridine (1.0 ml) at 0 $^{o}$C. After stirring of the reaction mixture for 3.0 h at room temperature, $H_2O$ (5.0 ml) was added. The aqueous layer was extracted with $CH_2Cl_2$, and the combined extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **11** (0.045 mmol, 32 mg, 45 %) as yellow solids.

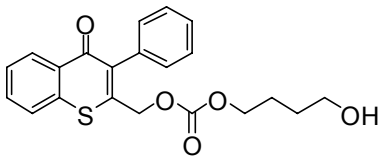
**11**



Yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.50 (1H, *J* = 7.3 Hz, d), 8.18 (1H, *J* = 7.9 Hz, d), 8.10 (1H, *J* = 7.9 Hz, d), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.67-7.60 (2H, m), 7.56-7.52 (1H, m), 7.50-7.43 (5H, m), 7.42-7.37 (1H, m), 7.34-7.27 (2H, m), 7.24-7.21 (2H, m), 5.10 (2H, s), 5.00 (2H, s), 4.23-4.17 (4H, m), 1.82-1.77 (4H, m). $^{13}$C-NMR ($CDCl_3$) δ: 179.21, 178.44, 154.36, 154.16, 145.30, 144.76, 144.07, 140.56, 136.57, 136.18, 134.83, 134.70, 133.32, 131.61, 131.02, 130.70, 129.80, 129.54, 129.36, 129.10, 128.97, 128.70, 128.53, 128.32, 127.80, 126.49, 123.21, 68.18, 68.07, 66.84, 60.79, 25.01, 24.98. IR ($CHCl_3$) 1752, 1669, 1620, 1592, 1442, 1315, 1243, 1223, 1217, 1211, 1208, 1163, 1031, 791, 769, 761, 751, 737, 732, 700, 669.

HRMS(FAB) calcd for $C_{38}H_{30}O_{10}S_2$($M^+$+H) 711.1359; found: 711.1367.

**12**

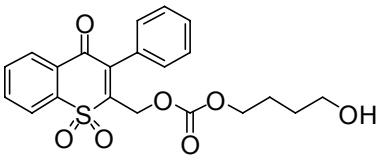


Yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.51 (1H, *J* = 7.3 Hz, d,), 7.64-7.63 (2H, m), 7.56-7.53 (1H, m), 7.47-7.46 (2H, m), 7.41-7.40 (1H, m), 7.24-7.23 (2H, m), 5.01 (2H, s), 4.22 (2H, *J* = 6.7 Hz, t,), 3.69 (2H, *J* = 6.4 Hz, t,), 1.83-1.77 (2H, m), 1.69-1.63 (2H, m). $^{13}$C-NMR ($CDCl_3$) δ: 179.23, 154.43, 145.31, 136.59, 136.19, 134.70, 131.60, 131.03, 129.55, 129.39, 128.70, 128.32, 127.82, 126.43, 68.71, 66.82, 62.24, 28.78, 25.13. IR ($CHCl_3$) 1794, 1748, 1700, 1652, 1616, 1464, 1381, 1224, 1221, 1219, 1217, 1215, 1214, 1211, 1206, 1096, 916, 795, 791, 790, 788, 787, 785.

HRMS(FAB) calcd for $C_{21}H_{20}O_5S$($M^+$+H) 385.1110; found: 385.1108.

Oxidation of **12** was carried out under the same condition of the synthesis of **2**.
Yield 85 %.

**13**

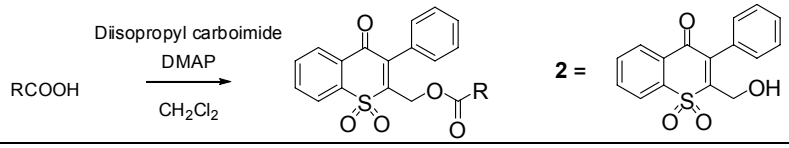


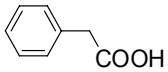
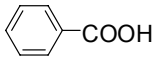

Yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.19 (1H, *J* = 7.9 Hz, d,), 8.11 (1H, *J* = 7.9 Hz, d,), 7.90 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd,), 7.49-7.48 (3H, m), 7.30-7.29 (2H, m), 5.10 (2H, s), 4.20 (2H, t, *J* = 6.4 Hz), 3.67 (2H, t, *J* = 6.4 Hz), 1.81-1.75 (2H, m), 1.68-1.62 (2H, m). $^{13}$C-NMR ($CDCl_3$) δ: 178.40, 154.18, 144.71, 144.05, 140.49, 134.79, 133.28, 130.64, 129.75, 129.06, 128.92, 128.48, 123.17, 68.66, 62.16, 60.66, 28.73, 25.00. IR ($CHCl_3$) 1750, 1669, 1589, 1443, 1396, 1314, 1265, 1228, 1224, 1223, 1220, 1217, 1215, 1213, 1210, 1208, 1205, 1163, 1141, 1071, 1031, 851, 802, 800, 795, 793, 791, 790, 788, 783, 780, 777.
HRMS(FAB) calcd for $C_{21}H_{20}O_7S(M^+ + Na)$ 439.0827; found: 439.0828.

**General procedure for the synthesis of ester derivatives 14.**

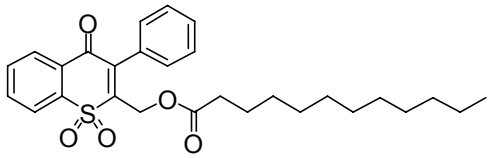
To a solution of **2** (0.12 mmol, 36 mg), DMAP (0.14 mmol, 18.0 mg) and carboxylic acid (0.08 mmol) were dissolved in $CH_2Cl_2$ (1.0 ml). diisopropyl carbodiimide (0.14 mmol, 18 mg) was added dropwise to a mixture at 0 $^oC$. After stirring of the reaction mixture for 3 h at room temperature, 1N HCl aq. (2.0 ml) was added. The aqueous layer was extracted with $CH_2Cl_2$, and the combined extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel to give **14**.

Protection of carboxylic acids.



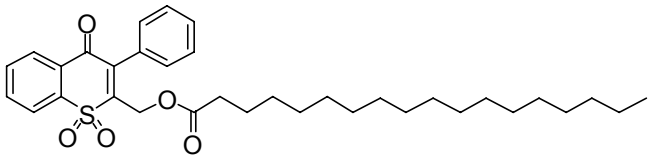

| Entry | Substrate | RCOOH | Temp. | time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | **14a** | $C_{11}H_{23}COOH$ | 0 $^oC$ to r. t. | 1.0 | 81 |
| 2 | **14b** | $C_{17}H_{35}COOH$ | 0 $^oC$ to r. t. | 1.0 | 73 |
| 3 | **14c** |  | 0 $^oC$ to r. t. | 1.0 | 76 |
| 4 | **14d** |  | 0 $^oC$ to r. t. | 1.0 | 78 |

**14a**



Yield 81 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.18 (1H, *J* = 7.9 Hz, d), 8.10 (1H, *J* = 7.9, 7.9 Hz, d), 7.88 (1H, *J* = 7.9, 7.9 Hz, dd), 7.77 (1H, *J* = 7.9, 7.9 Hz, dd), 7.47-7.46 (3H, m), 7.28-7.27 (2H, m), 5.03 (2H, s), 2.34 (2H, *J* = 7.3 Hz, t), 1.61-1.60 (2H, m), 1.28-1.25 (18H, m), 0.88 (3H, *J* = 7.0 Hz, t). $^{13}$C-NMR ($CDCl_3$) δ: 178.44, 172.72, 145.05, 144.31, 140.68, 134.73, 133.24, 130.96, 129.67, 129.02, 129.00, 128.91, 128.45, 123.14, 57.68, 33.90, 31.90, 29.59, 29.43, 29.32, 29.22, 29.05, 24.65, 22.68, 14.13. IR ($CHCl_3$) 1797, 1731, 1669, 1600, 1591, 1460,, 1375, 1270, 1221, 1211, 1159, 1140, 1129, 1101, 1072, 909, 865, 785, 770, 768, 755, 745, 730, 727, 669, 650.
HRMS(FAB) calcd for $C_{28}H_{34}O_5S(M^+ + Na)$ 505.2025; found: 505.2016

**14b**



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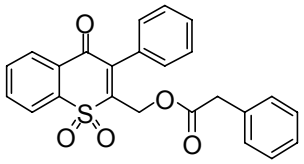
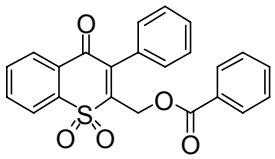
Yield 73 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.19 (1H, *J* = 7.9 Hz, d), 8.11 (1H, *J* = 7.9 Hz, d), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.47-7.47 (3H, m), 7.28-7.26 (2H, m), 5.03 (2H, s), 2.34 (2H, *J* = 7.6 Hz, t), 1.61-1.60 (2H, m), 1.28-1.25 (28H, m), 0.88 (3H, *J* = 6.7 Hz, t). $^{13}$C-NMR ($CDCl_3$) δ: 178.42, 172.70, 145.04, 144.29, 140.68, 134.70, 133.21, 130.92, 129.65, 129.00, 128.98, 128.90, 128.43, 123.13, 57.66, 33.88, 31.89, 29.67, 29.64, 29.62, 29.57, 29.42, 29.33, 29.20, 29.03, 24.63, 22.66, 14.10. IR ($CHCl_3$) 1794, 1725, 1668, 1602, 1589, 1454, 1379, 1374, 1267, 1222, 1208, 1163, 1140, 1127, 1095, 1071, 911, 863, 787, 776, 765, 758, 745, 730, 726, 669, 650.
HRMS(FAB) calcd for $C_{34}H_{46}O_5S(M^+ + Na)$ 589.2964; found: 589.2962

**14c**



Yield 76 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.18 (1H, *J* = 7.9 Hz, d), 8.11 (1H, *J* = 7.9 Hz, d), 7.88 (1H, *J* = 7.9, 7.9 Hz, dd), 7.76 (1H, *J* = 7.9, 7.9 Hz, dd), 7.43-7.41 (1H, m), 7.35-7.33 (4H, m), 7.29-7.25 (3H, m), 7.16-7.15 (2H, m), 5.02 (2H, s), 3.67 (2H, s). $^{13}$C-NMR ($CDCl_3$) δ: 178.35, 170.41, 144.66, 144.52, 140.65, 134.71, 133.24, 133.22, 130.76, 129.62, 129.43, 128.96, 128.90, 128.58, 128.38, 127.24, 123.14, 58.11, 40.85. IR ($CHCl_3$) 1743, 1668, 1589, 1495, 1455, 1443, 1375, 1312, 1264, 1222, 1209, 1162, 1138, 1074, 1030, 1002, 909, 851, 788, 772, 759, 745, 732, 669, 650.
HRMS(FAB) calcd for $C_{24}H_{18}O_5S(M^+ + Na)$ 441.0773; found: 441.0770.

**14d**

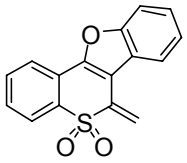


Yield 78 %, yellow solid. $^{1}$H-NMR ($CDCl_3$/TMS) δ: 8.20 (1H, *J* = 7.9 Hz, d), 8.12 (1H, *J* = 7.9 Hz, d), 8.07 (2H, *J* = 7.3 Hz, d), 7.89 (1H, *J* = 7.9, 7.9 Hz, dd), 7.78 (1H, *J* = 7.9, 7.9 Hz, dd), 7.57 (1H, *J* = 7.3 Hz, t), 7.45-7.43 (5H, m), 7.33-7.28 (2H, m), 5.29 (2H, s). $^{13}$C-NMR ($CDCl_3$) δ: 178.50, 165.49, 144.96, 144.48, 140.76, 134.77, 133.44, 133.26, 130.91, 129.97, 129.77, 129.05, 129.03, 129.02, 128.95, 128.57, 128.48, 123.16, 58.59. IR ($CHCl_3$) 1742, 1668, 1589, 1465, 1380, 1313, 1222, 1209, 1162, 1097, 913, 788, 777, 761, 750, 737, 733, 669, 650.
HRMS(FAB) calcd for $C_{23}H_{16}O_5S(M^+ + Na)$ 427.0616; found: 427.0620.

**General procedure for photoreaction.**

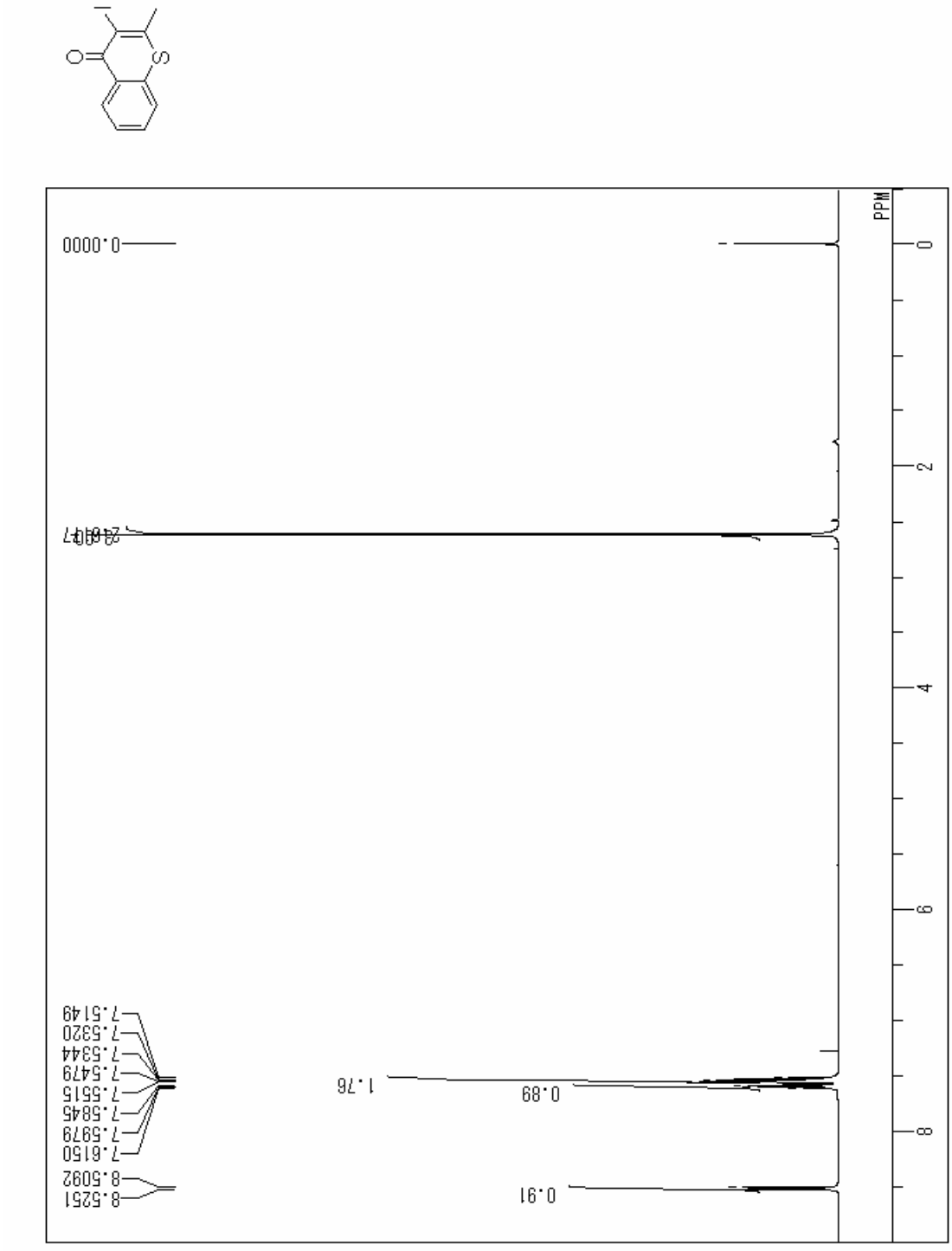
Irradiation reactions were carried out using an ultra-high pressure mercury lump (SX-UI-500H, USHIO) as the light source. A solution of the substrate in MeOH or $CD_3OD$ ($2\times10^{-2}$ M) was purged with $N_2$ and irradiated through pyrex vessel or UV-monochrometer (SPG-120UV, SHIMADZU). The yield was determined by $^1$H-NMR spectroscopy. In addition, the reaction mixture was concentrated *in vacuo* and purification by flash chromatography on silica gel to give alcohol and the corresponding **10**.

**10**




Yellow solid. $^1$H-NMR ($CDCl_3$/TMS) δ: 8.02 (1H, *J* = 7.9 Hz, d), 7.91 (1H, *J* = 7.9 Hz, d), 7.68 (1H, *J* = 7.9 Hz, d), 7.63 (1H, *J* = 7.9, 7.9 Hz, dd), 7.53 (1H, *J* = 7.9 Hz, d), 7.48 (1H, *J* = 7.9, 7.9 Hz, dd), 7.36 (1H, *J* = 7.9, 7.9 Hz, dd), 7.31 (1H, *J* = 7.9, 7.9 Hz, dd), 6.62 (1H, *J* = 1.8 Hz, d), 6.38 (1H, *J* = 1.8 Hz, d).$^{13}$C-NMR ($CDCl_3$) δ:155.03, 146.92, 141.04, 136.30, 133.27, 129.46, 126.61, 125.77, 125.05, 124.49, 124.44, 123.93, 120.33, 119.63, 112.20, 111.54. IR ($CHCl_3$) 1309, 1223, 1212, 1207, 1155, 1129, 789, 781, 758. HRMS(EI) calcd for $C_{16}H_{10}O_3S$, 282.0351; found: 282.0351.

**4**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8.5251
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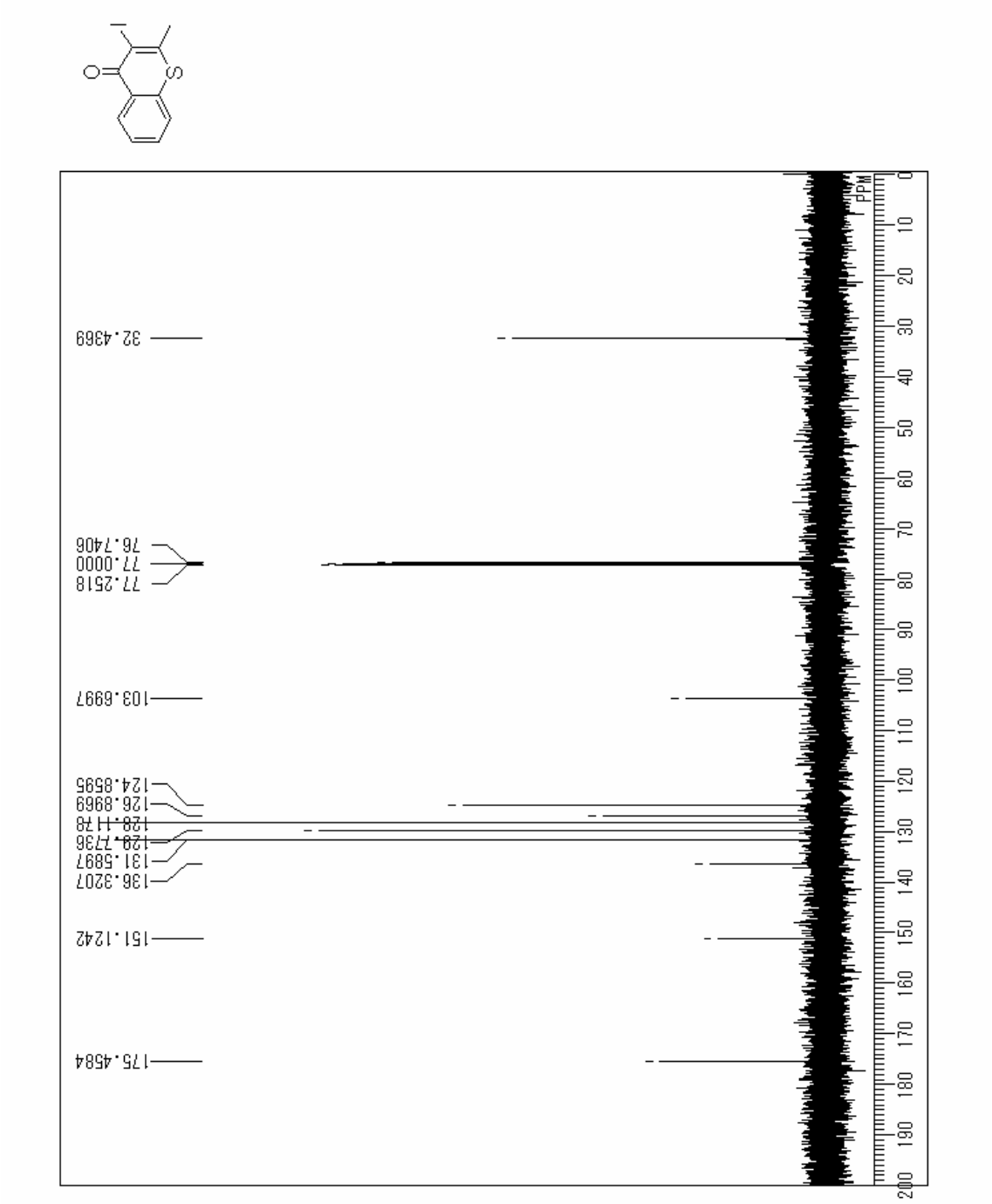
0.89
0.91
PPM
0
2
4
6
8

**4**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77.0000
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126.8969
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128.7736
131.5897
136.3207
151.1242
175.4584
PPM
0
10
20
30
40
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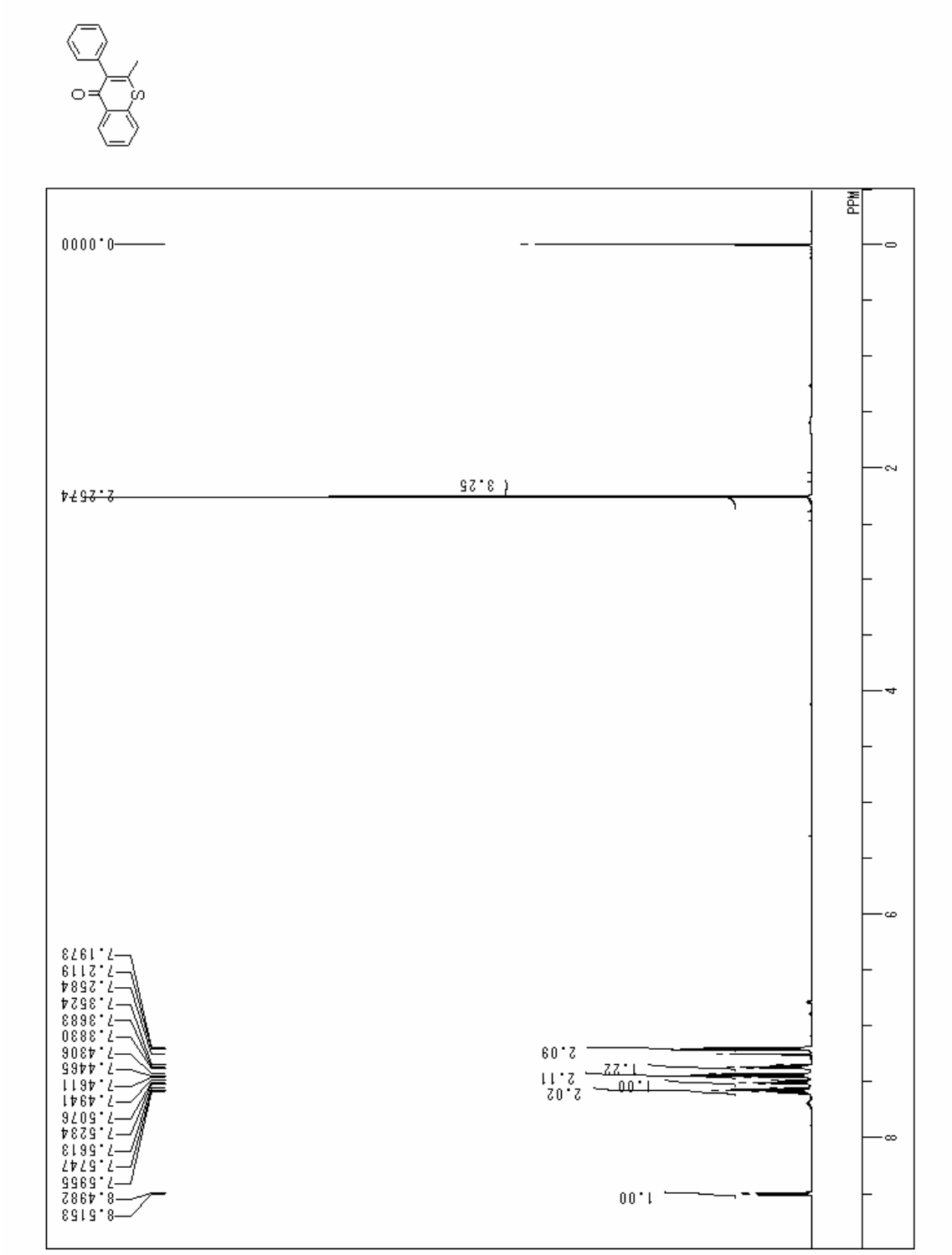
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

**5**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8.25
7.1978
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7.3524
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7.4306
7.4465
7.4611
7.4941
7.5076
7.5234
7.5618
7.5747
7.5955
8.4982
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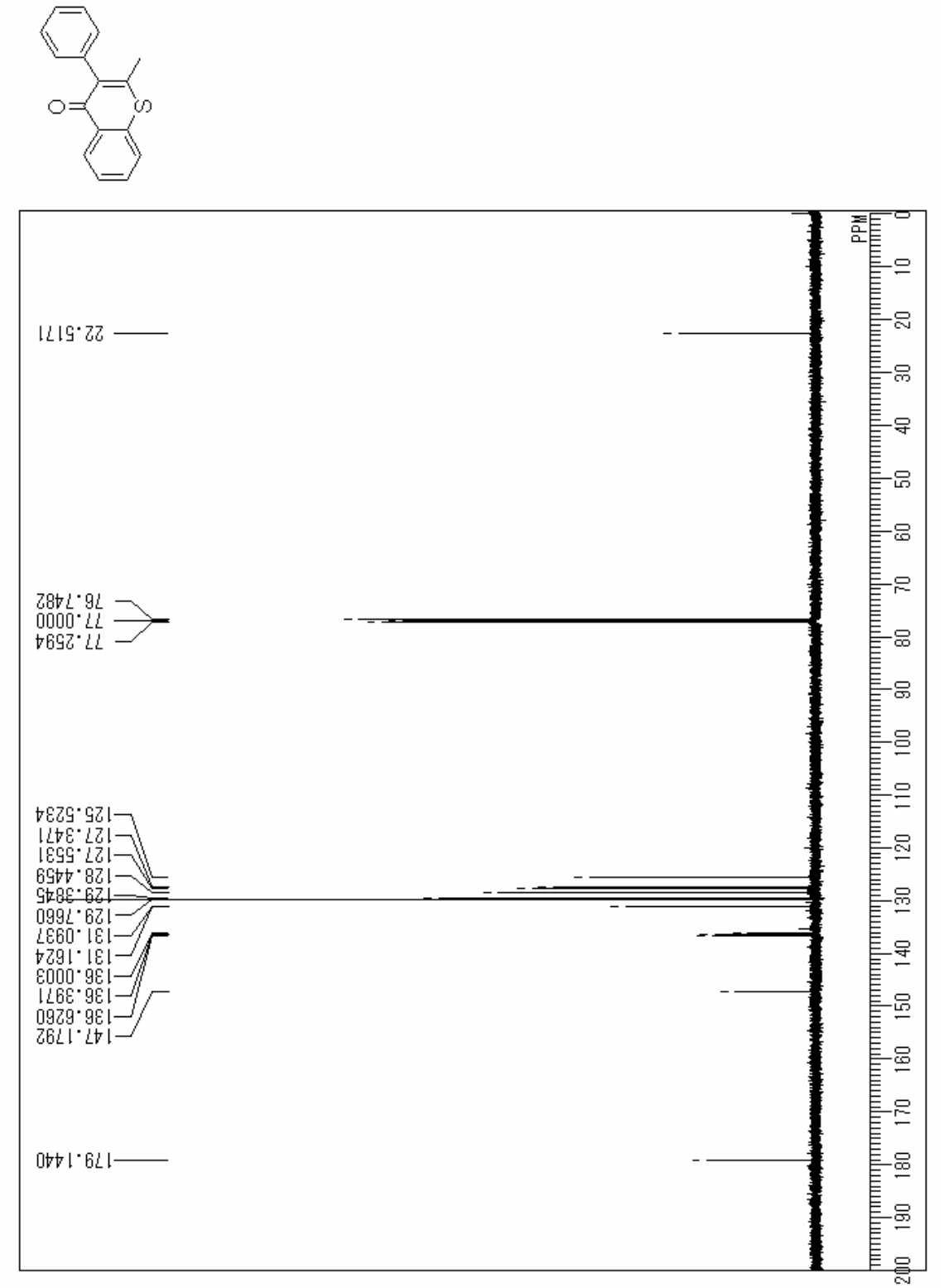
1.00
2.02
1.00
PPM
0
2
4
6
8

**5**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127.5531
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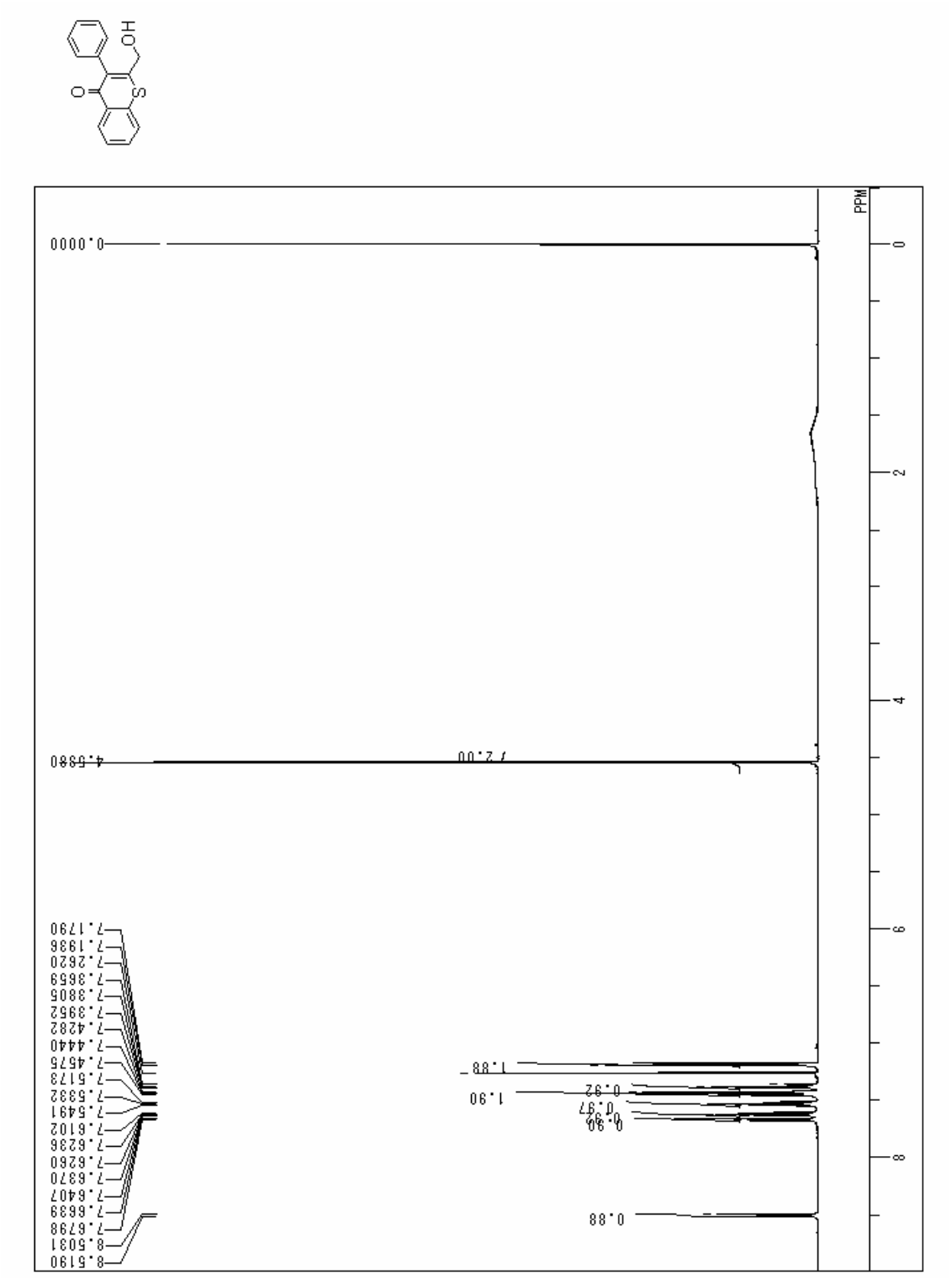
129.3845
129.7660
131.0937
131.1624
136.0003
136.3971
136.6260
147.1792
179.1440
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

**1**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O
S
PPM
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4
6
8
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7.2.00
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0.97
0.90
0.88
7.1790
7.1938
7.2620
7.3659
7.3805
7.3952
7.4282
7.4440
7.4575
7.5178
7.5382
7.5491
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7.6260
7.6370
7.6407
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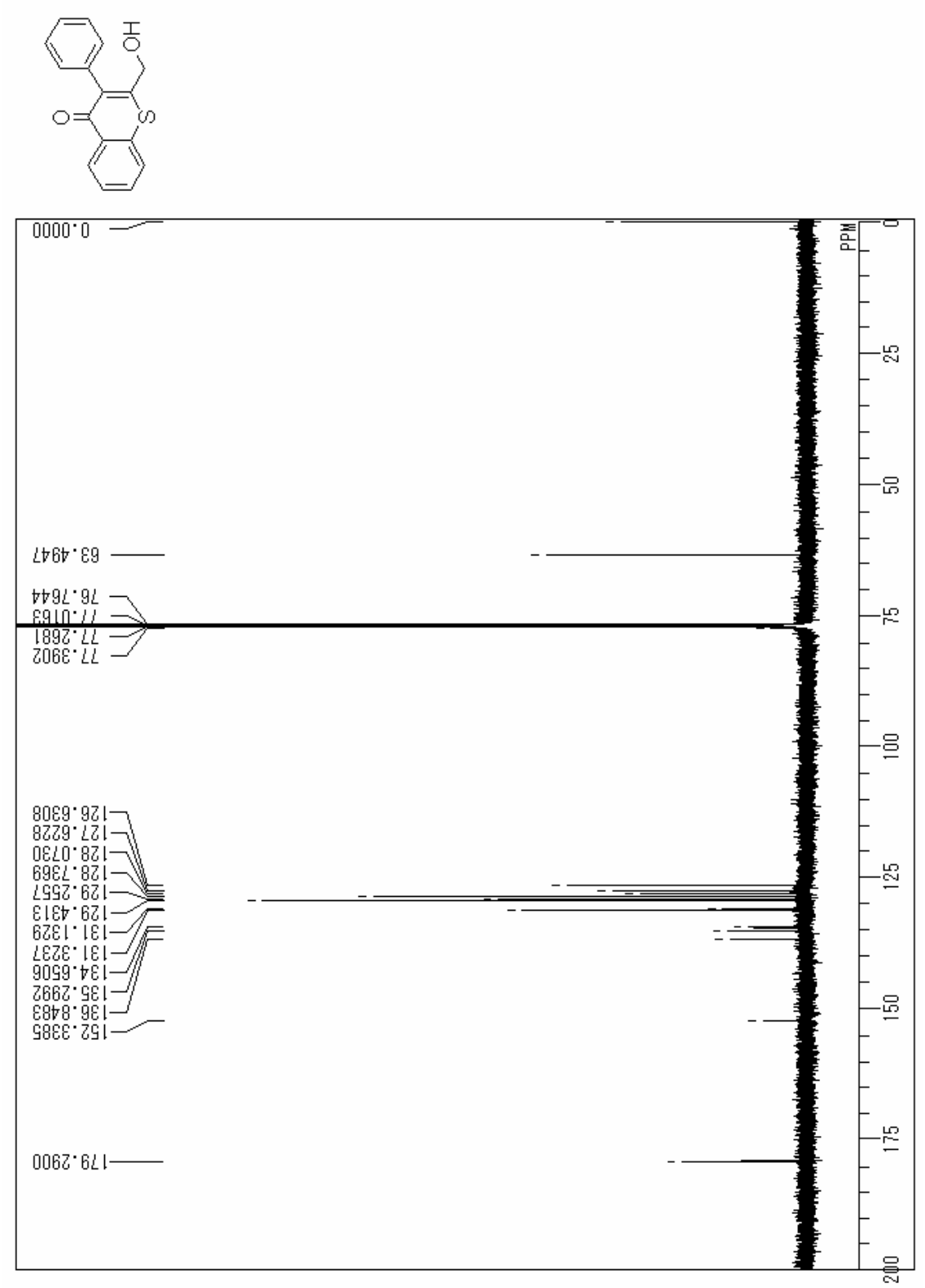
7.6798
8.5031
8.5190

**1**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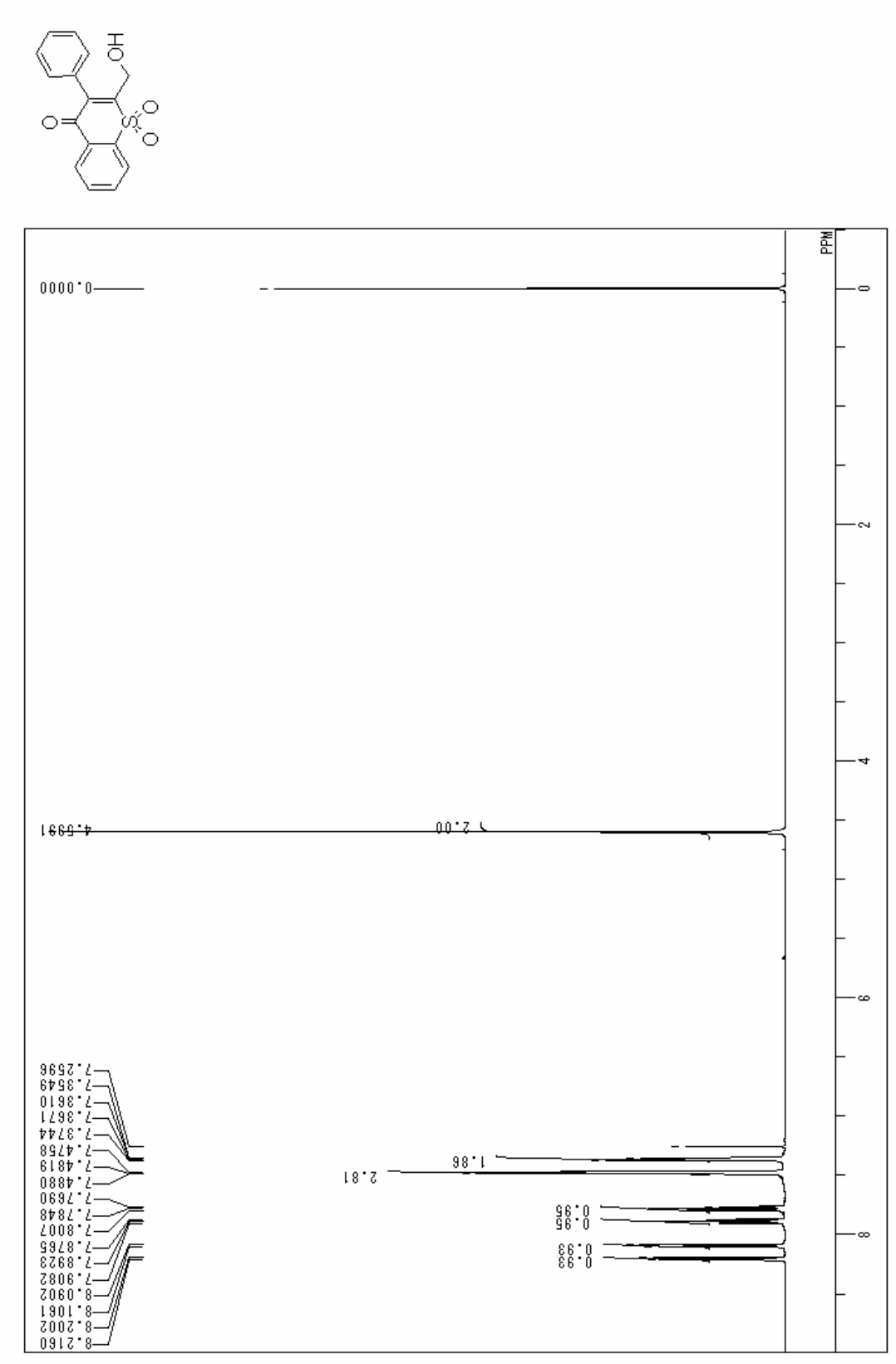
129.2557
129.4913
131.1329
131.3237
134.6506
135.2992
136.8483
152.3385
179.2900
PPM
0
25
50
75
100
125
150
175
200

**2**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O
O
O
PPM
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2
4
6
8
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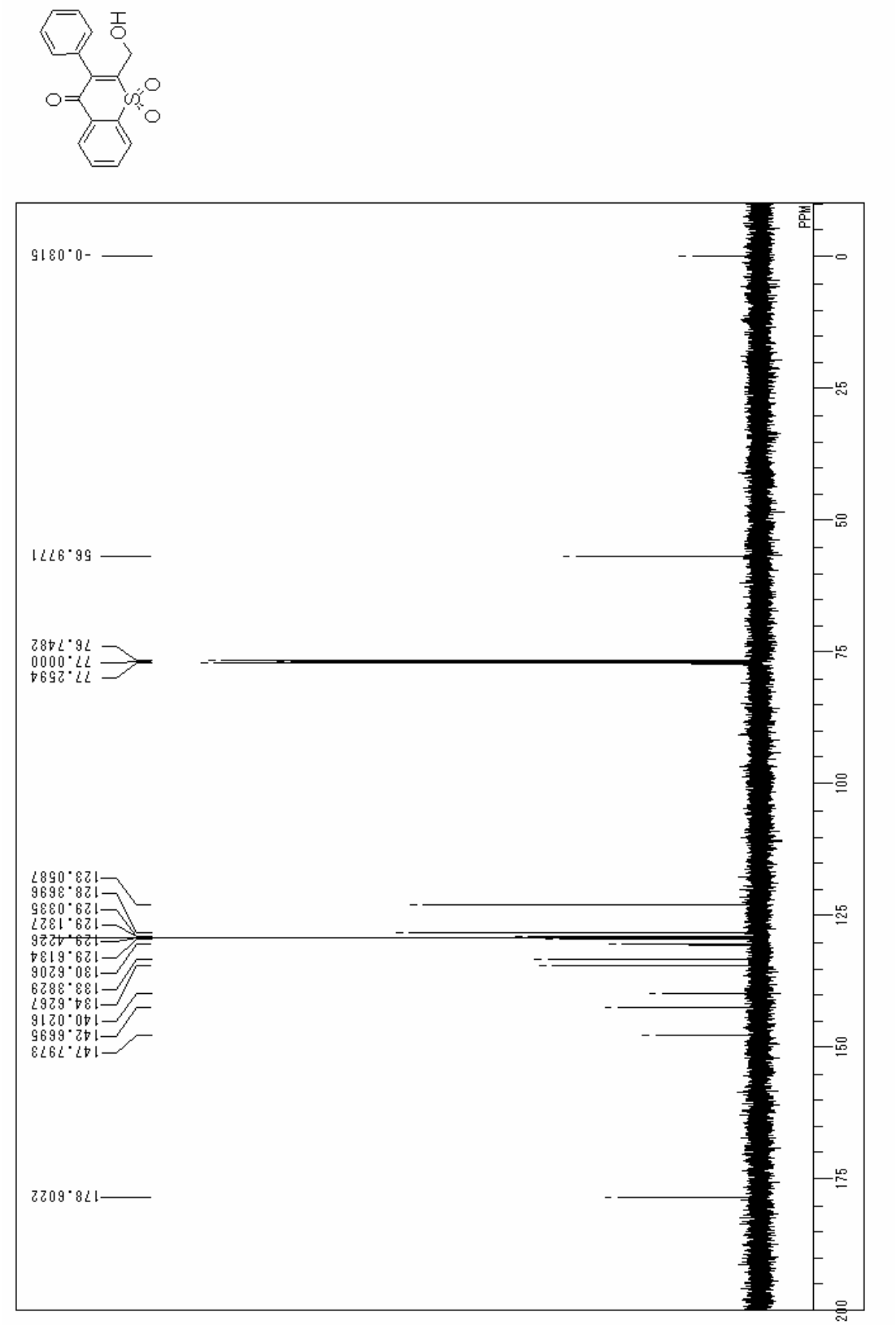
2.00
1.86
2.81
0.96
0.95
0.93
0.93
7.2596
7.3549
7.3810
7.3871
7.3744
7.4758
7.4819
7.4880
7.7690
7.7848
7.8007
7.8765
7.8928
7.9082
8.0902
8.1061
8.2002
8.2160

**2**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O
O
S
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129.1827
129.4226
129.6184
130.6206
133.3829
134.6267
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178.6022
PPM
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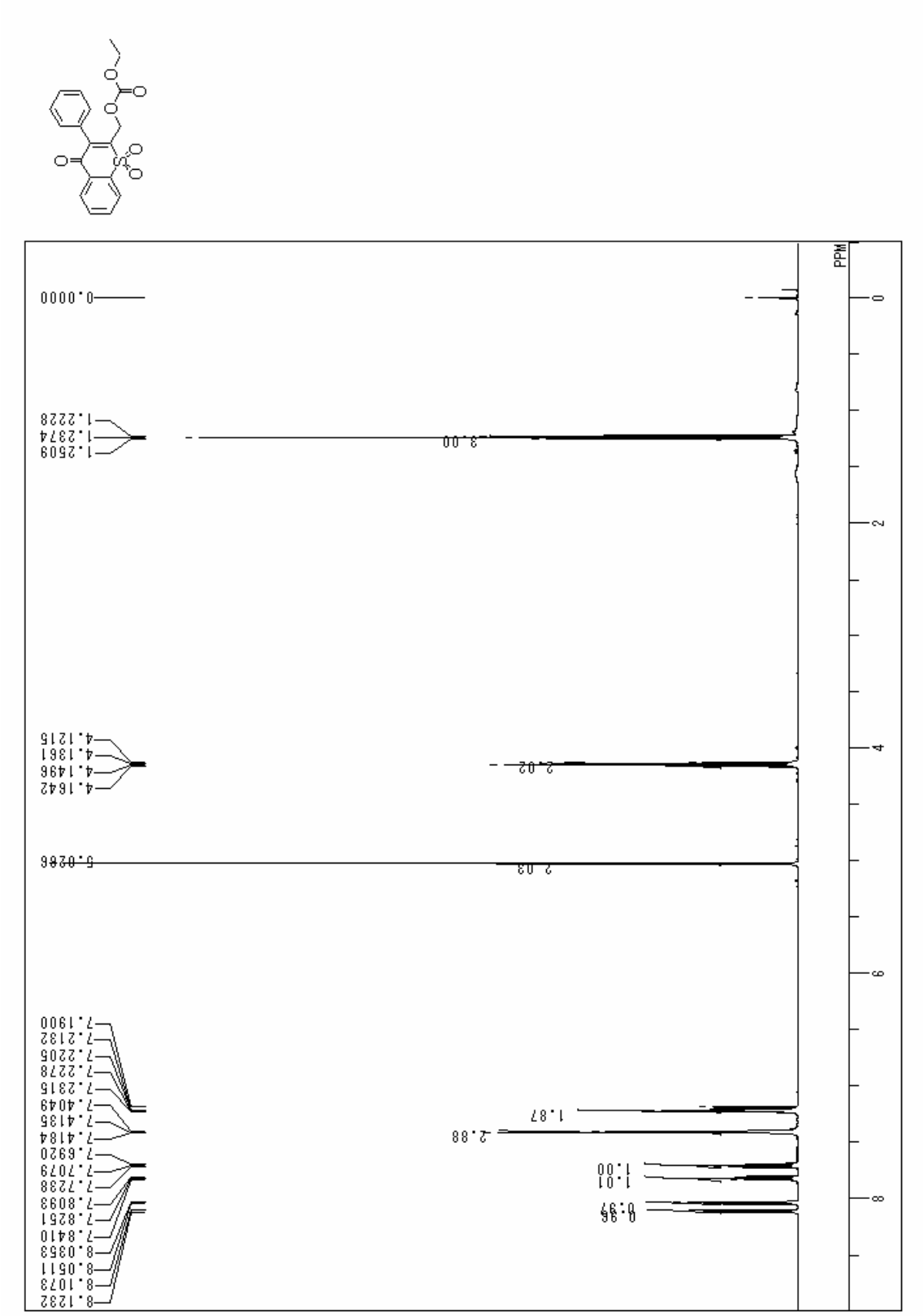
50
75
100
125
150
175
200

**9a**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8
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3.00
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4.1361
4.1496
4.1642
2.02
5.0286
2.08
7.1900
7.2182
7.2205
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7.2315
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7.4135
7.4184
7.6920
7.7079
7.7238
7.8098
7.8251
7.8410
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8.0511
8.1078
8.1282
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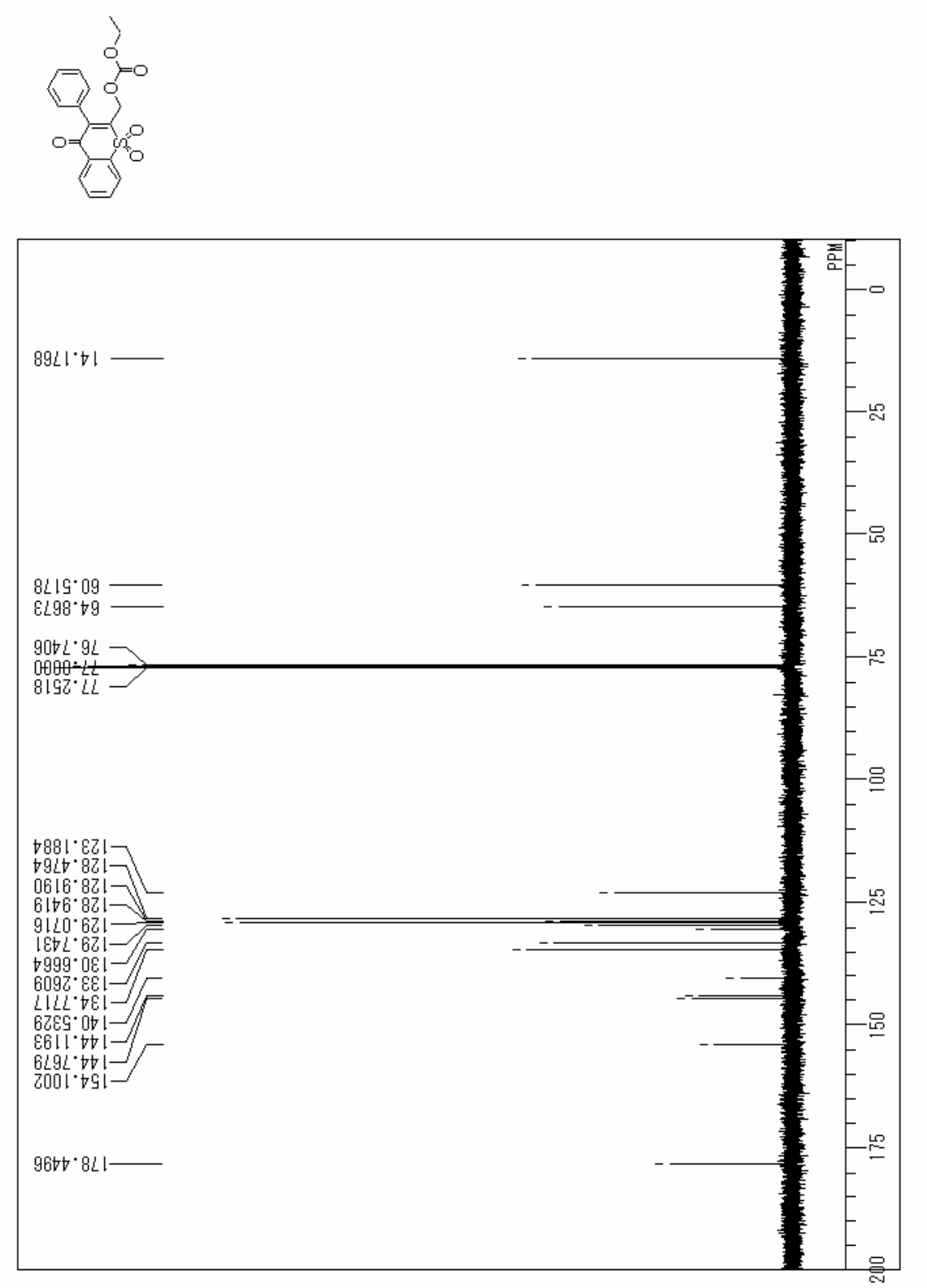
1.00
1.01
0.96
0.97

**9a**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129.7431
130.6664
133.2609
134.7717
140.5329
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75
100
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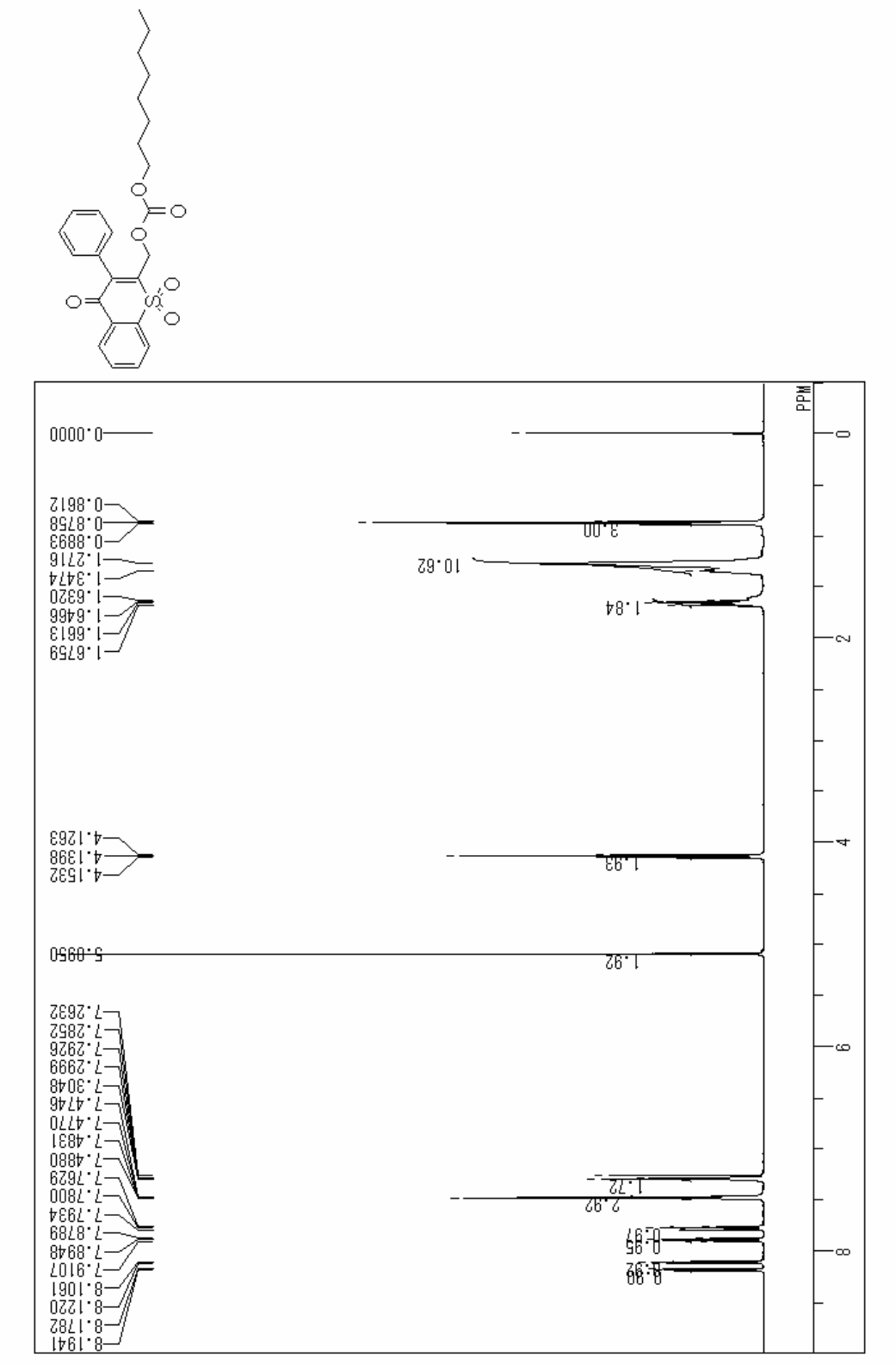
150
175
200

**9b**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1.6320
1.6466
1.6613
1.6759
4.1263
4.1398
4.1532
5.0950
7.2632
7.2852
7.2926
7.2999
7.3048
7.4746
7.4770
7.4831
7.4880
7.7629
7.7800
7.7934
7.8789
7.8948
7.9107
8.1061
8.1220
8.1782
8.1941
3.00
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1.93
1.92
2.92
1.72
PPM
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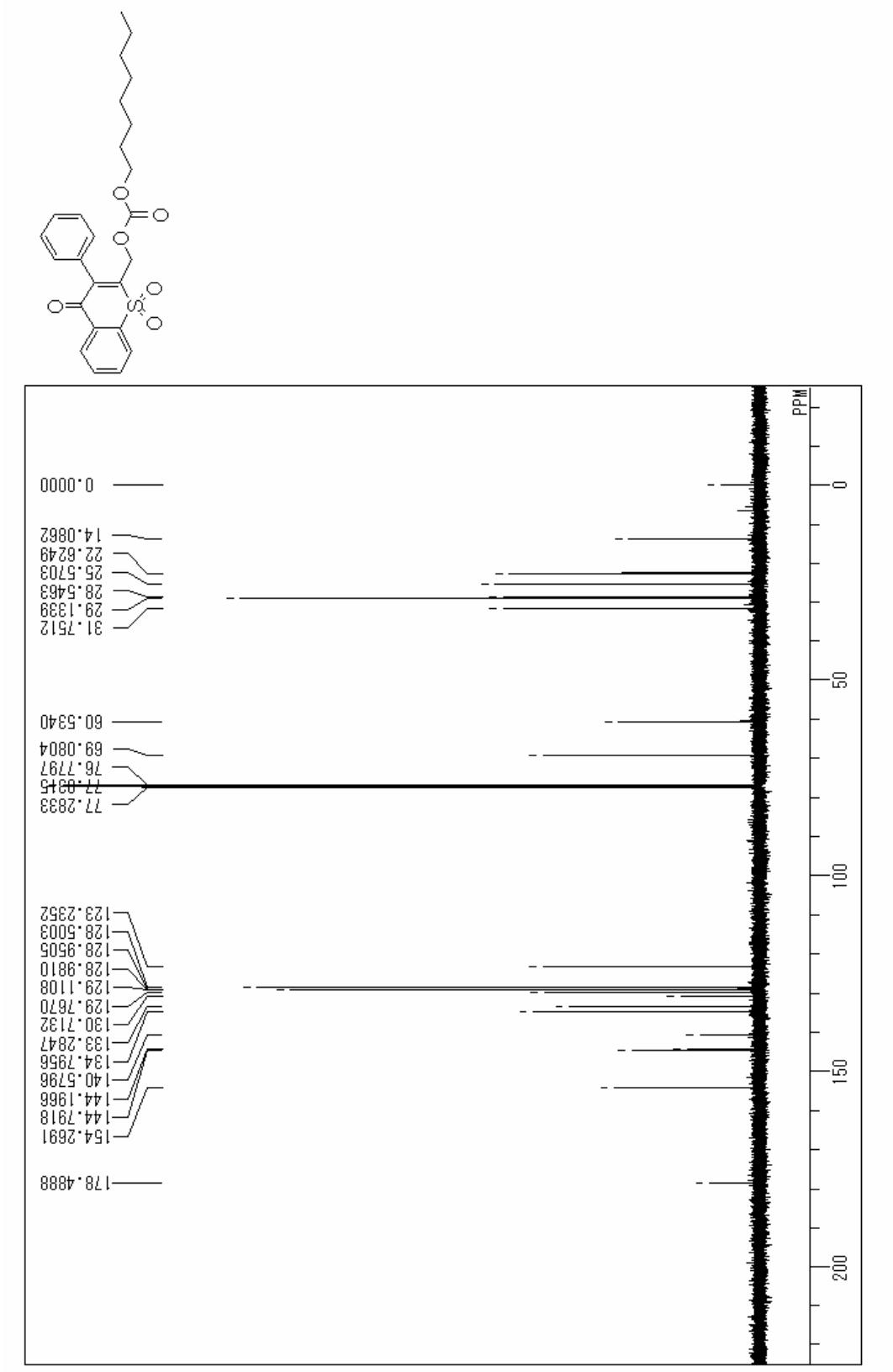
2
4
6
8

**9b**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77.0315
77.2833
123.2352
128.5003
128.9505
128.9810
129.1108
129.7670
130.7132
133.2847
134.7956
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154.2691
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PPM
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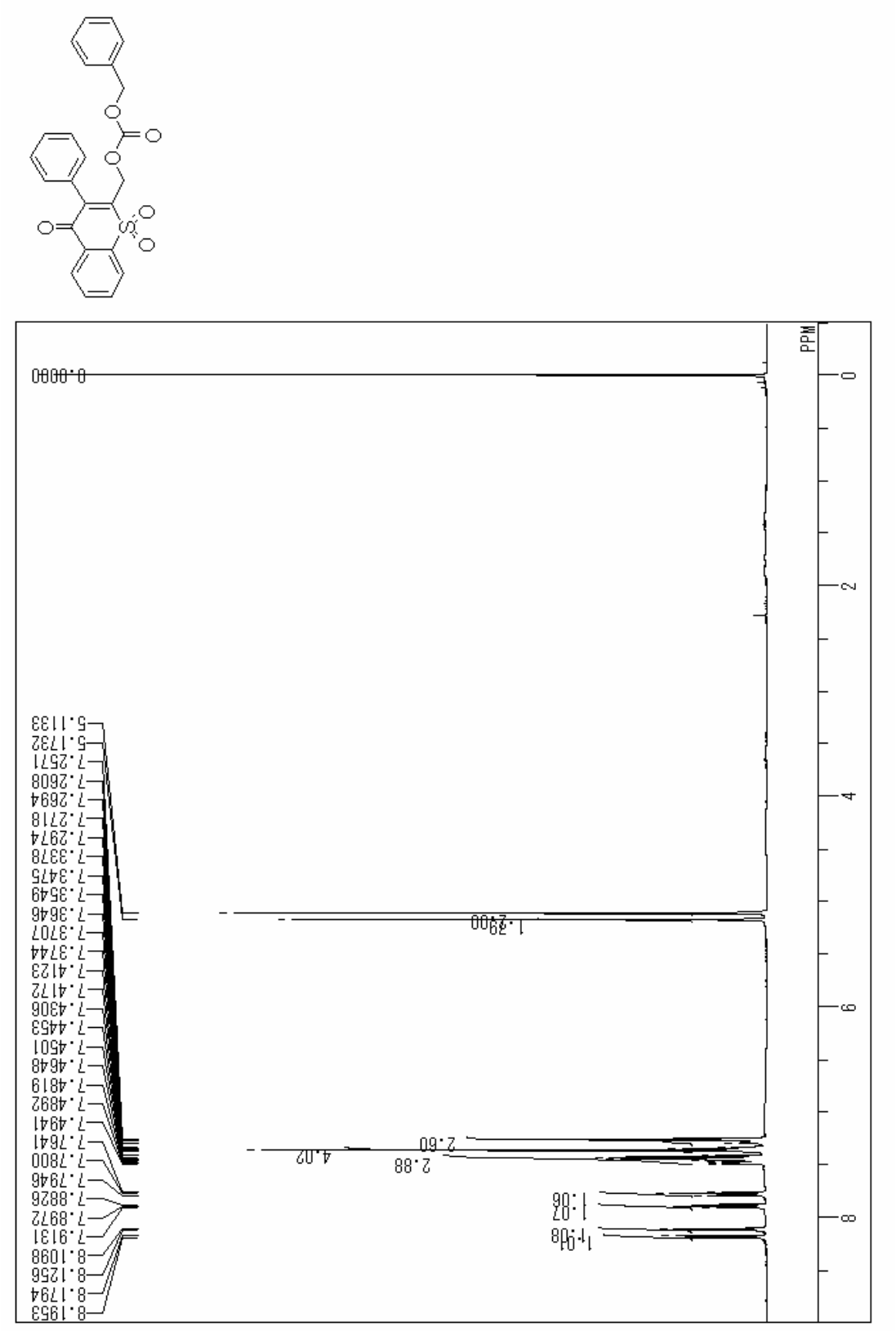
150
200

**9c**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4
6
8
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1.0700
2.8800
4.0200
2.6000
8.1953
8.1794
8.1256
8.1098
7.9131
7.8972
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7.7946
7.7800
7.7641
7.4941
7.4892
7.4819
7.4648
7.4501
7.4453
7.4306
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7.3646
7.3549
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7.2694
7.2608
7.2571
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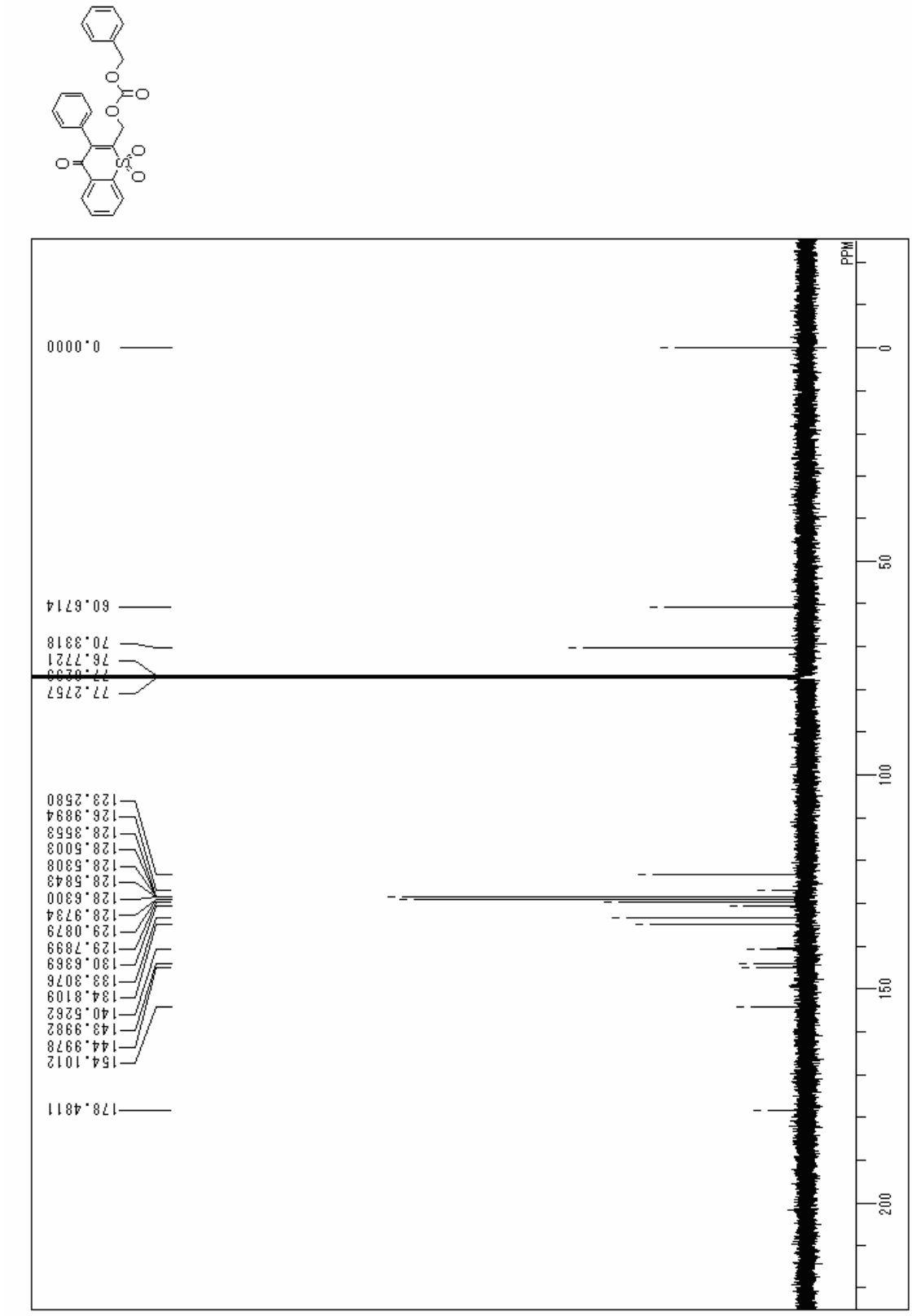
5.1133

**9c**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128.5308
128.5843
128.6300
128.9734
129.0879
129.7899
130.6869
133.8076
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144.9978
154.1012
178.4811
PPM
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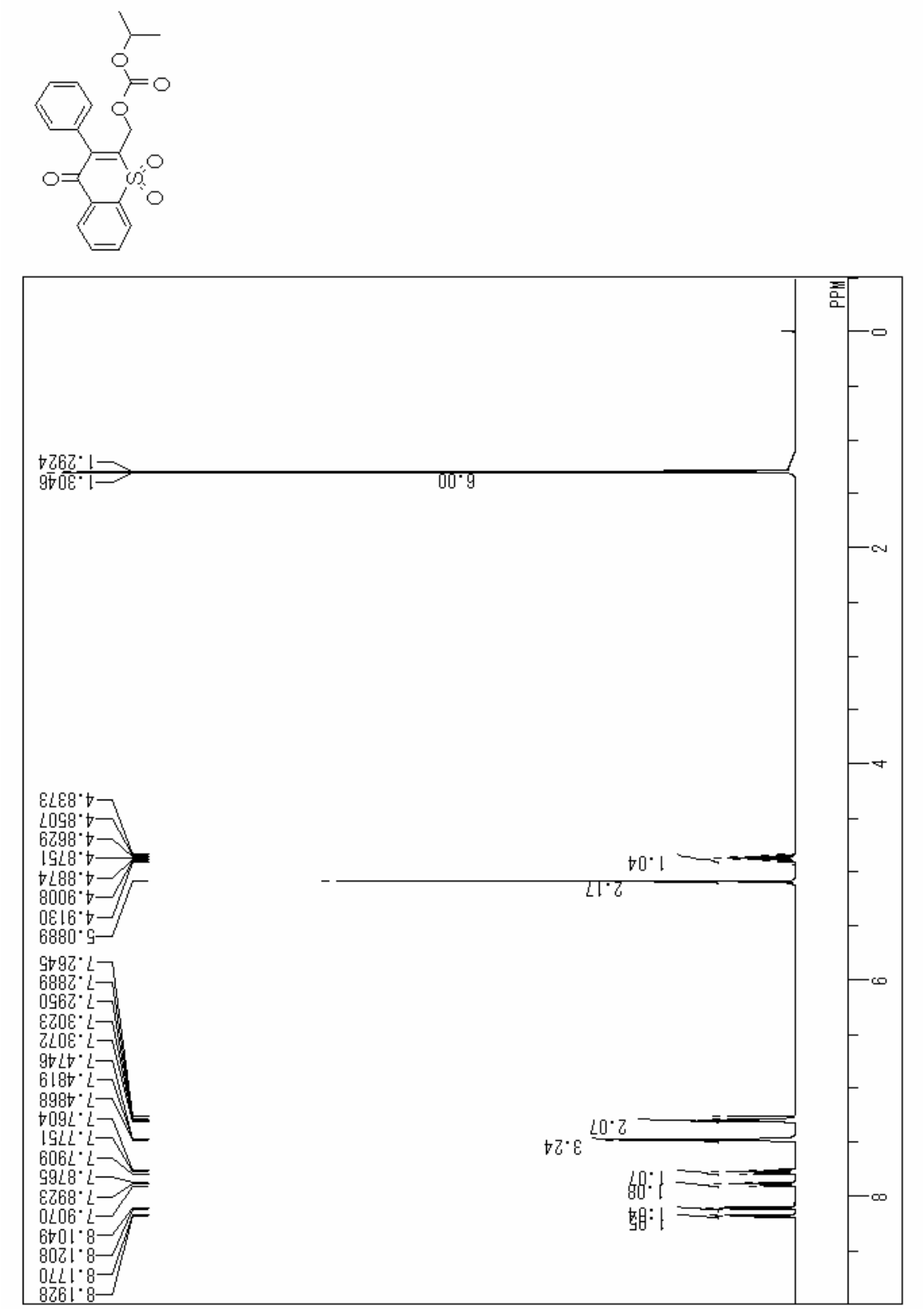
100
150
200

**9d**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4
6
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4.8629
4.8751
4.8874
4.9008
4.9130
5.0889
1.04
2.17
7.2645
7.2889
7.2950
7.3023
7.3072
7.4746
7.4819
7.4868
7.7604
7.7751
7.7909
7.8765
7.8928
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8.1049
8.1208
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8.1928
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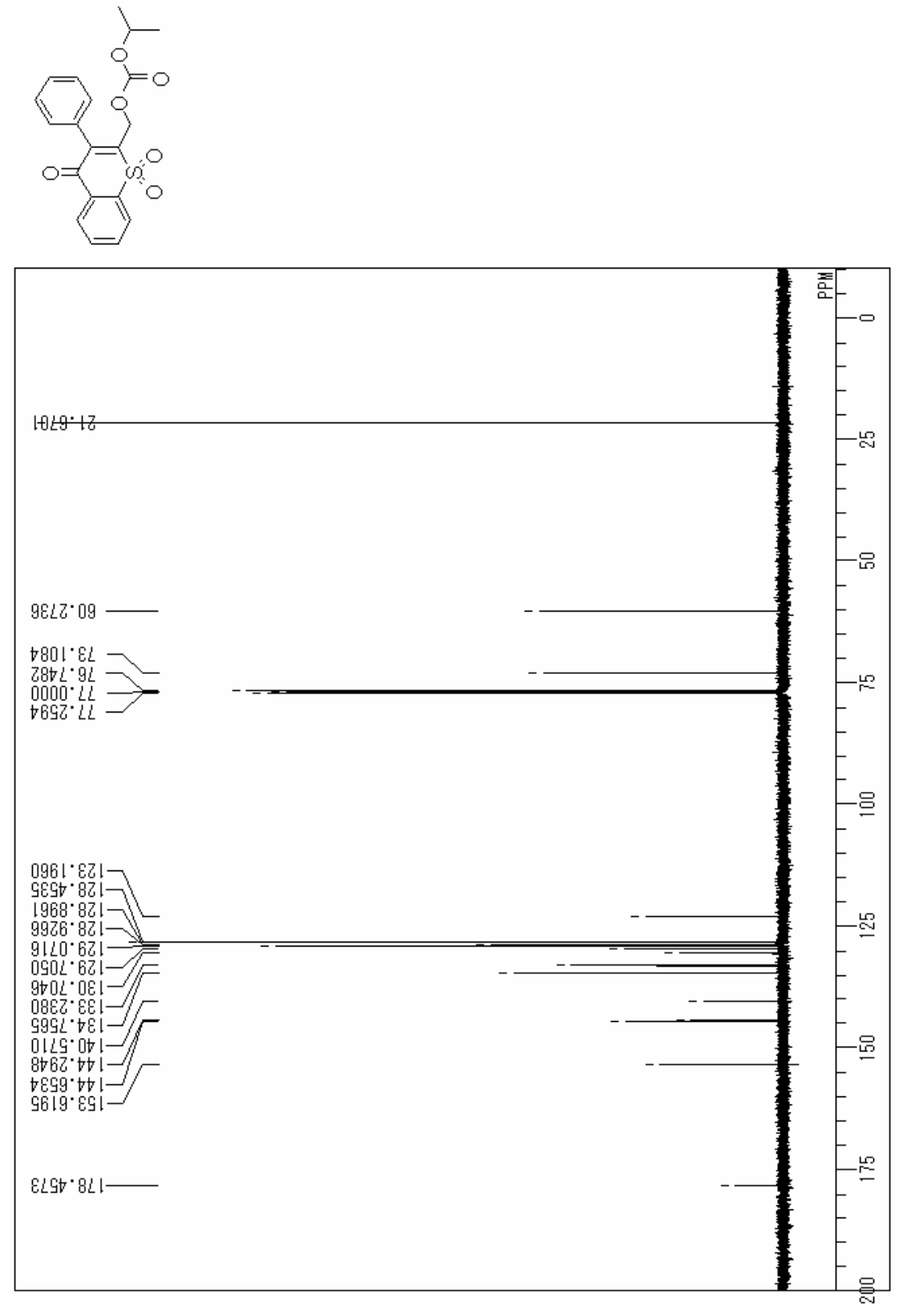
3.24
1.08
1.07
1.85

**9d**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129.7050
130.7046
133.2380
134.7565
140.5710
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75
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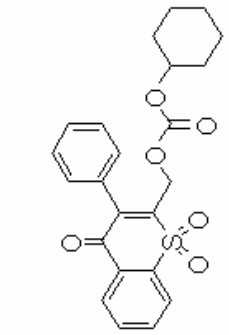
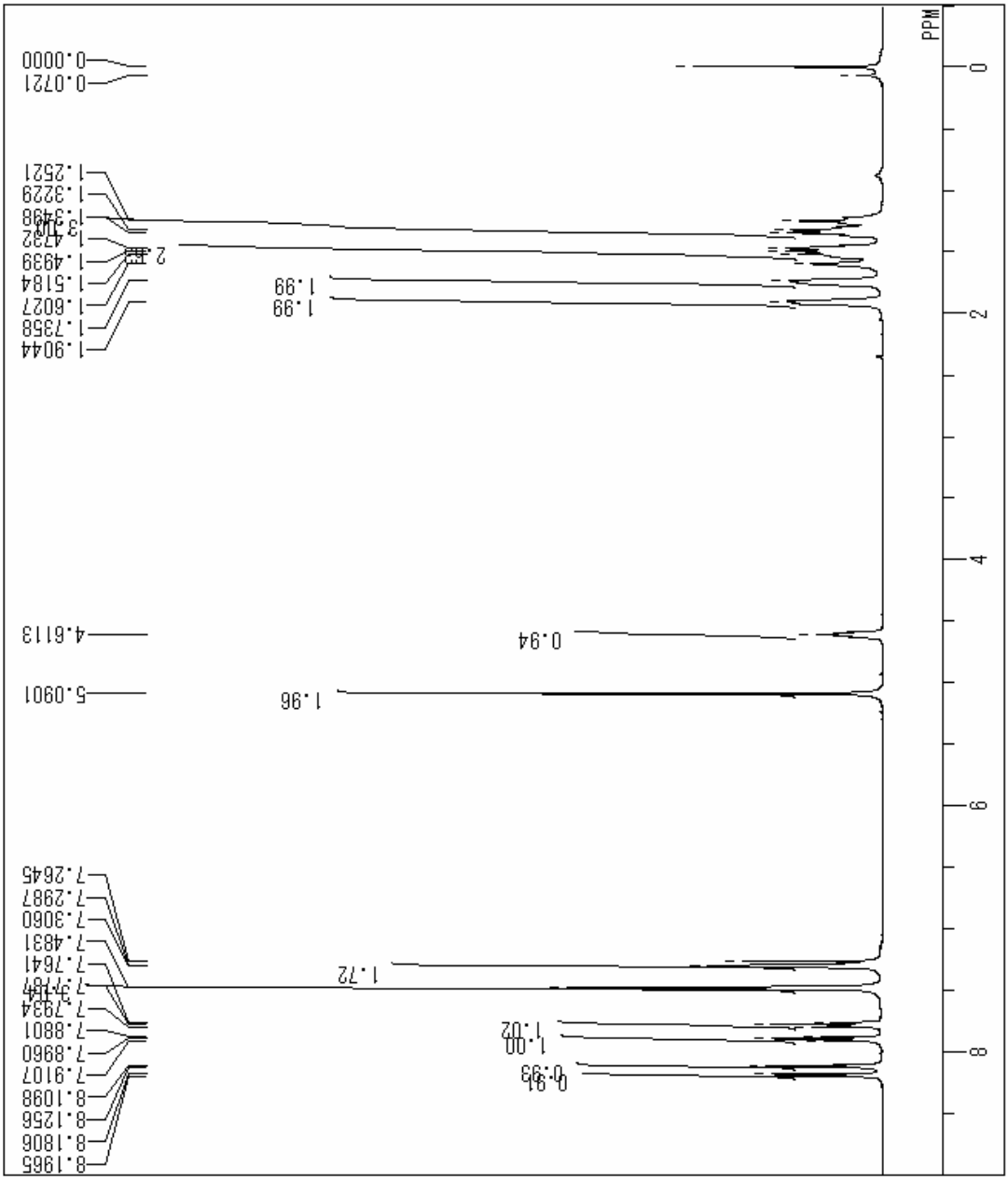
150
175
200

**9e**

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1.4732
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1.5184
1.6027
1.7358
1.9044
1.99
1.99
4.6113
0.94
5.0901
1.96
7.2645
7.2987
7.3060
7.4831
7.7641
1.72
7.7934
7.8801
7.8960
7.9107
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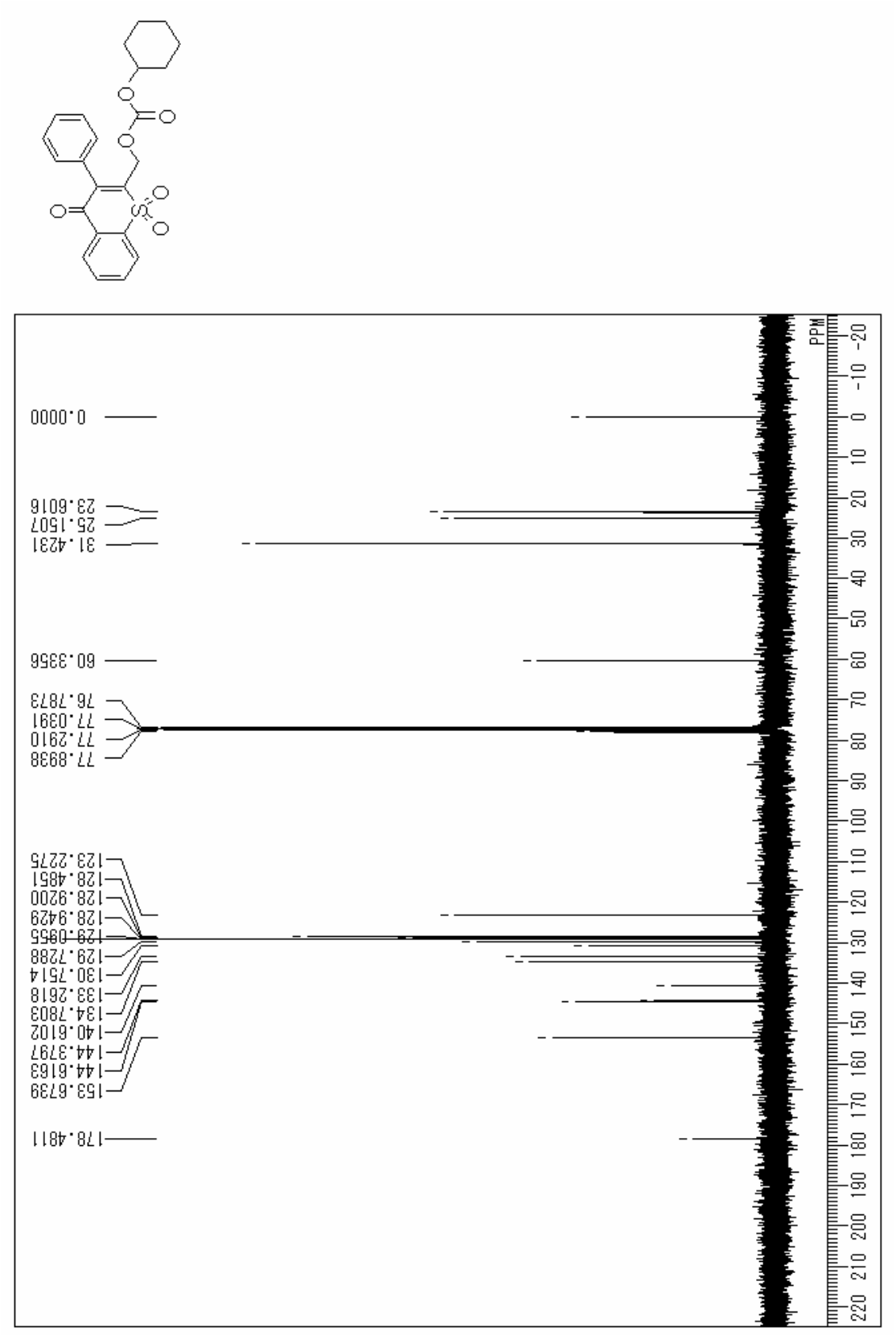
8.1256
8.1806
8.1965
1.00
1.02
0.93
0.91

**9e**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129.7288
130.7514
133.2618
134.7803
140.6102
144.3797
144.6163
153.6739
178.4811
PPM
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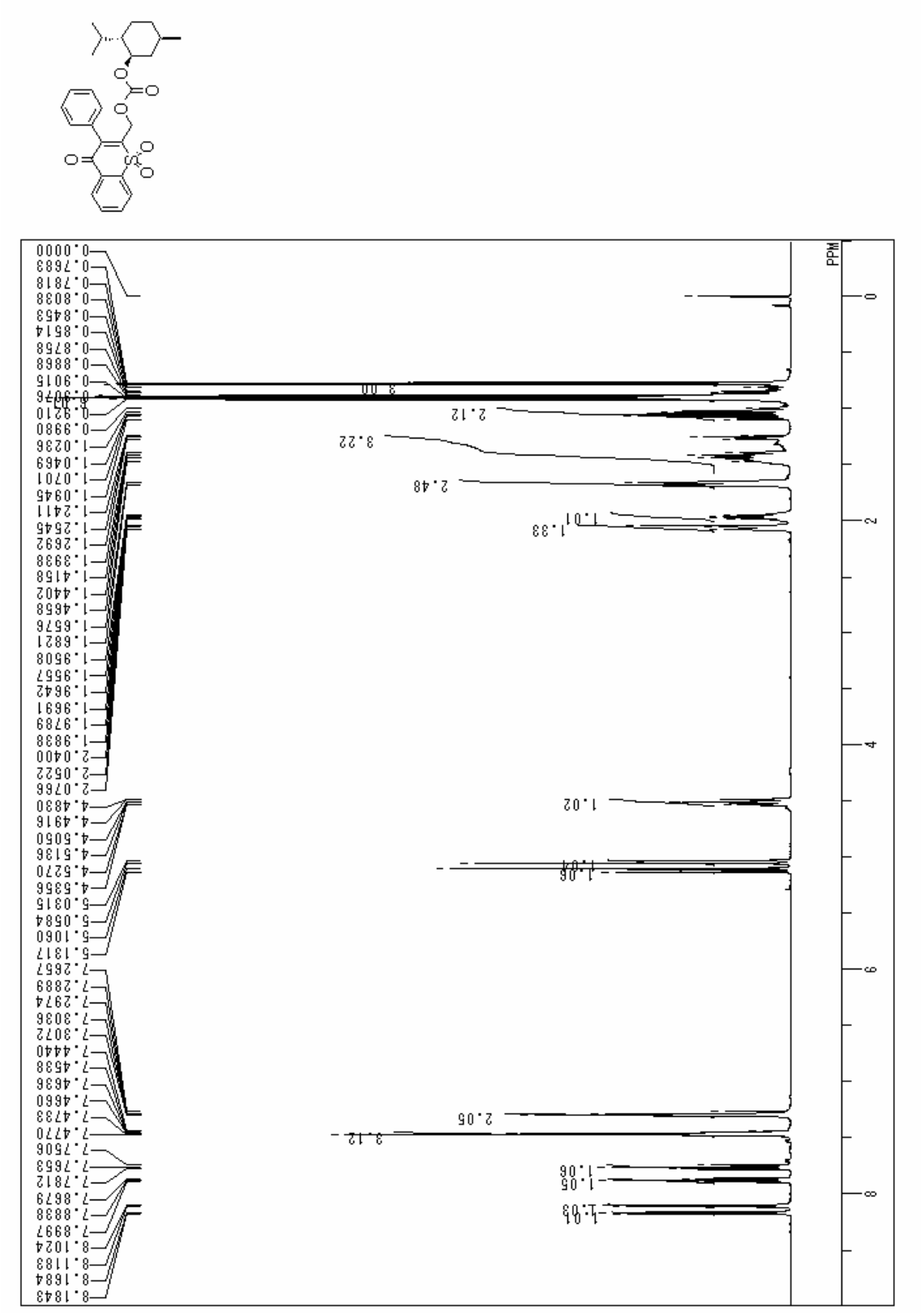
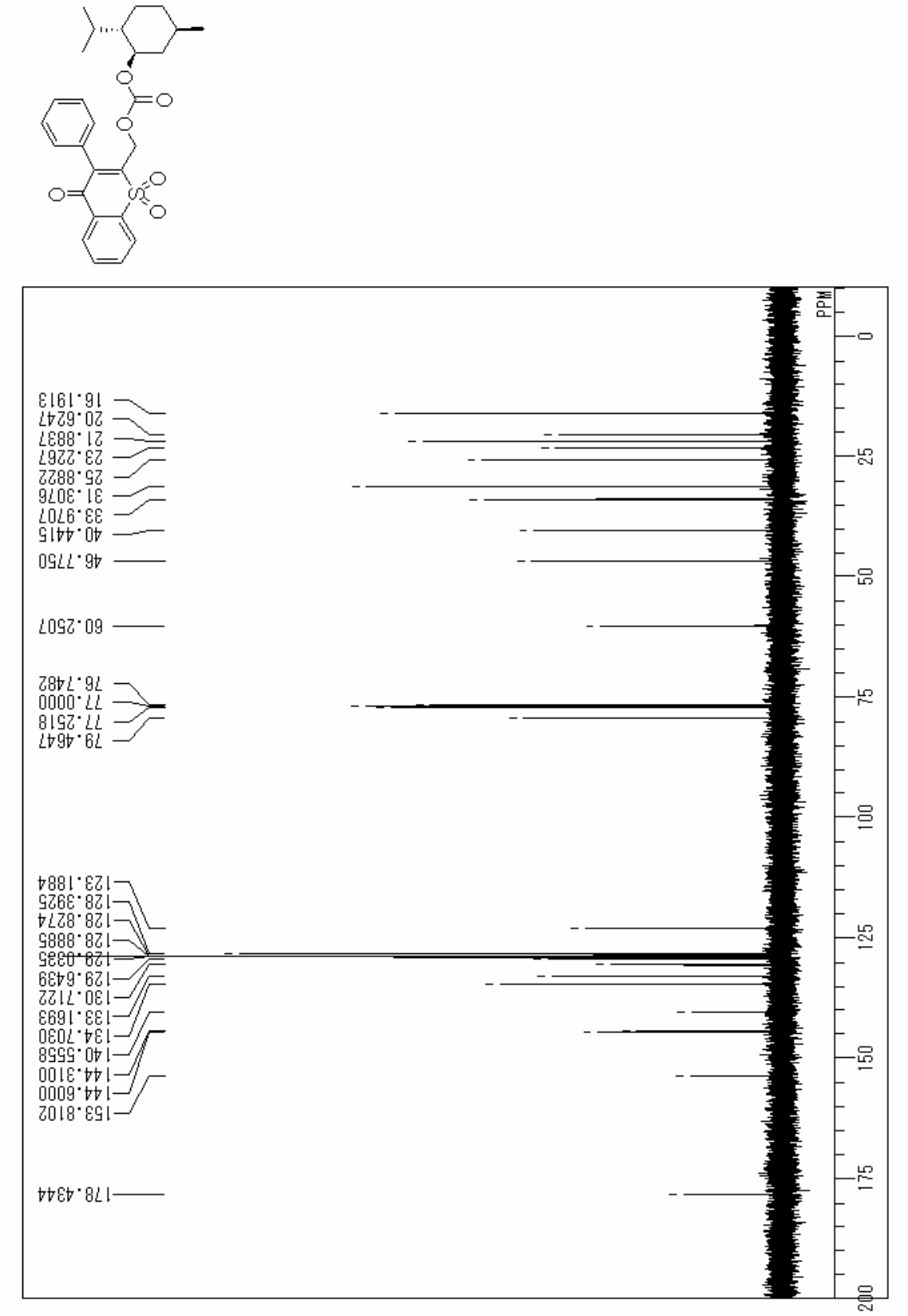
**9f**



**9f**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76.7482
77.0000
77.2518
79.4647
123.1884
128.3925
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128.8885
129.0335
129.6439
130.7122
133.1693
134.7030
140.5558
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153.8102
178.4344
PPM
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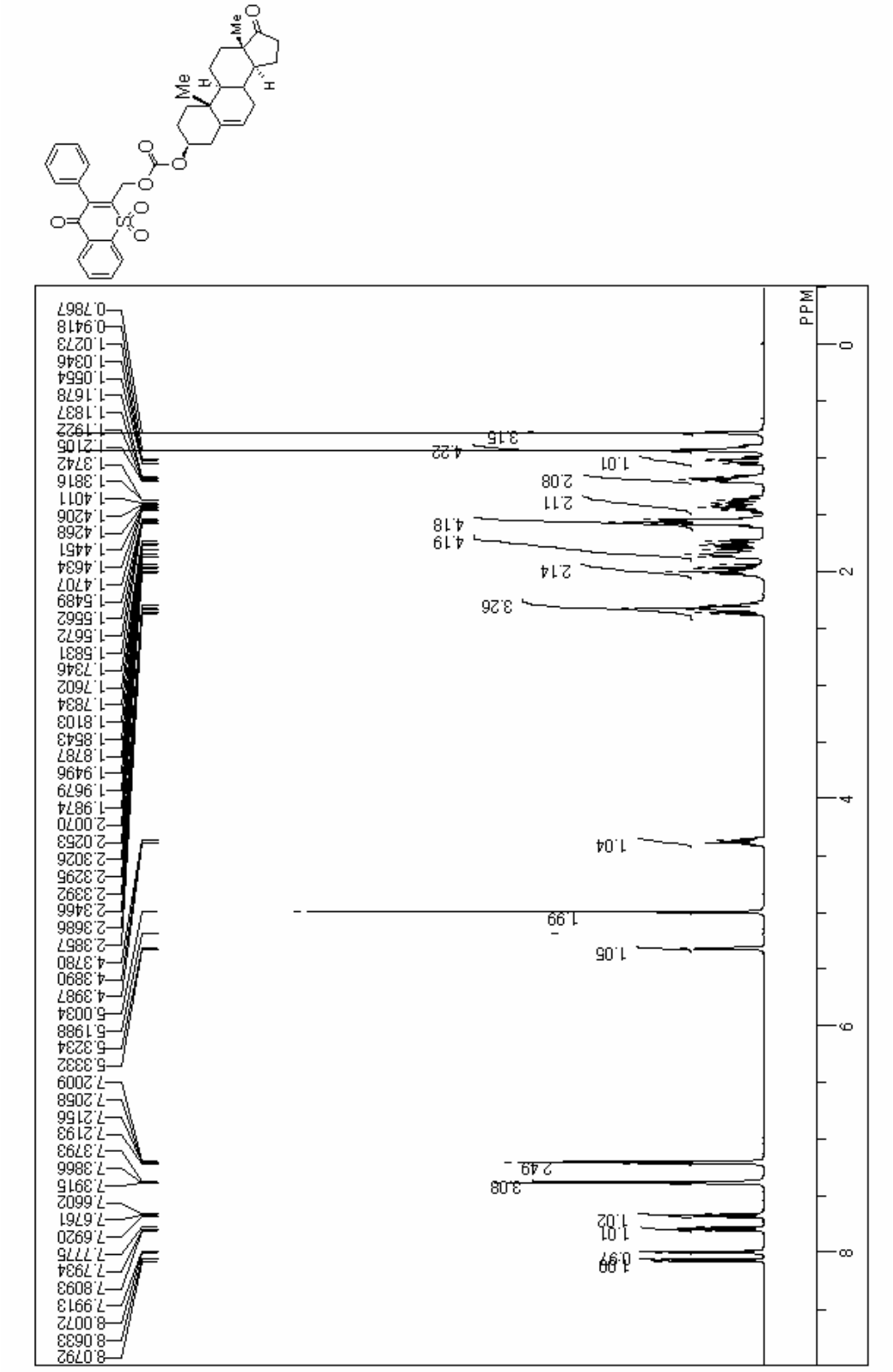
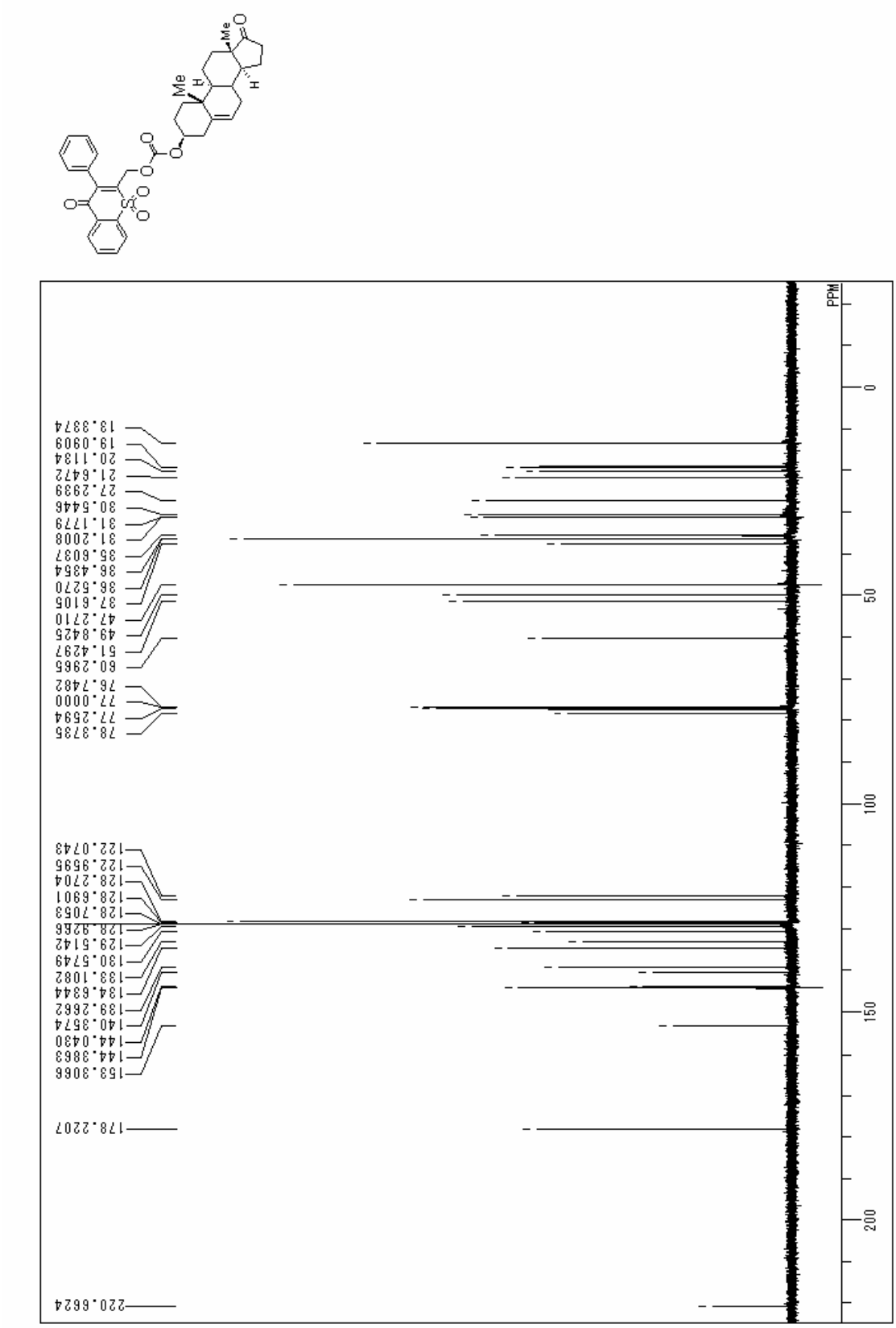
25
50
75
100
125
150
175
200

**9g**


Me
H
Me
H
O
O
O
O
O
O
S
O
O
PPM
0
2
4
6
8
3.15
4.22
1.01
2.08
2.11
4.18
4.19
2.14
3.26
1.04
1.99
1.05
2.49
3.08
1.02
1.01
0.97
1.99

**9g**


Me
H
Me
H
O
O
O
O
O
S
O
O
PPM
0
50
100
150
200
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19.0909
20.1184
21.6472
27.2989
30.5446
31.1779
31.2008
35.6037
36.4864
36.5270
37.6105
47.2710
49.8425
51.4297
60.2965
76.7482
77.0000
77.2694
78.8786
122.0748
122.9595
128.2704
128.6901
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129.5142
130.5749
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144.0430
144.3863
158.3066
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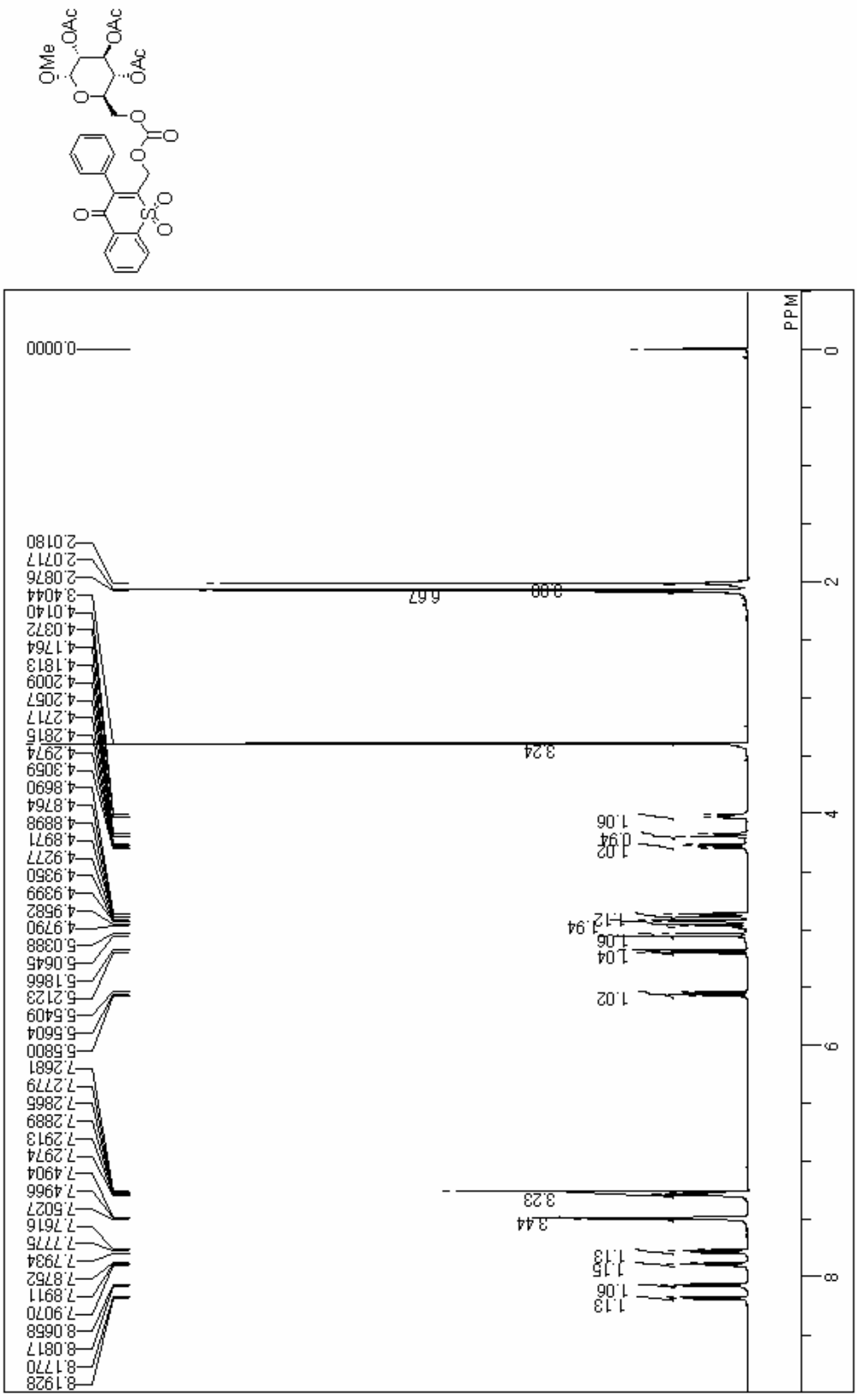
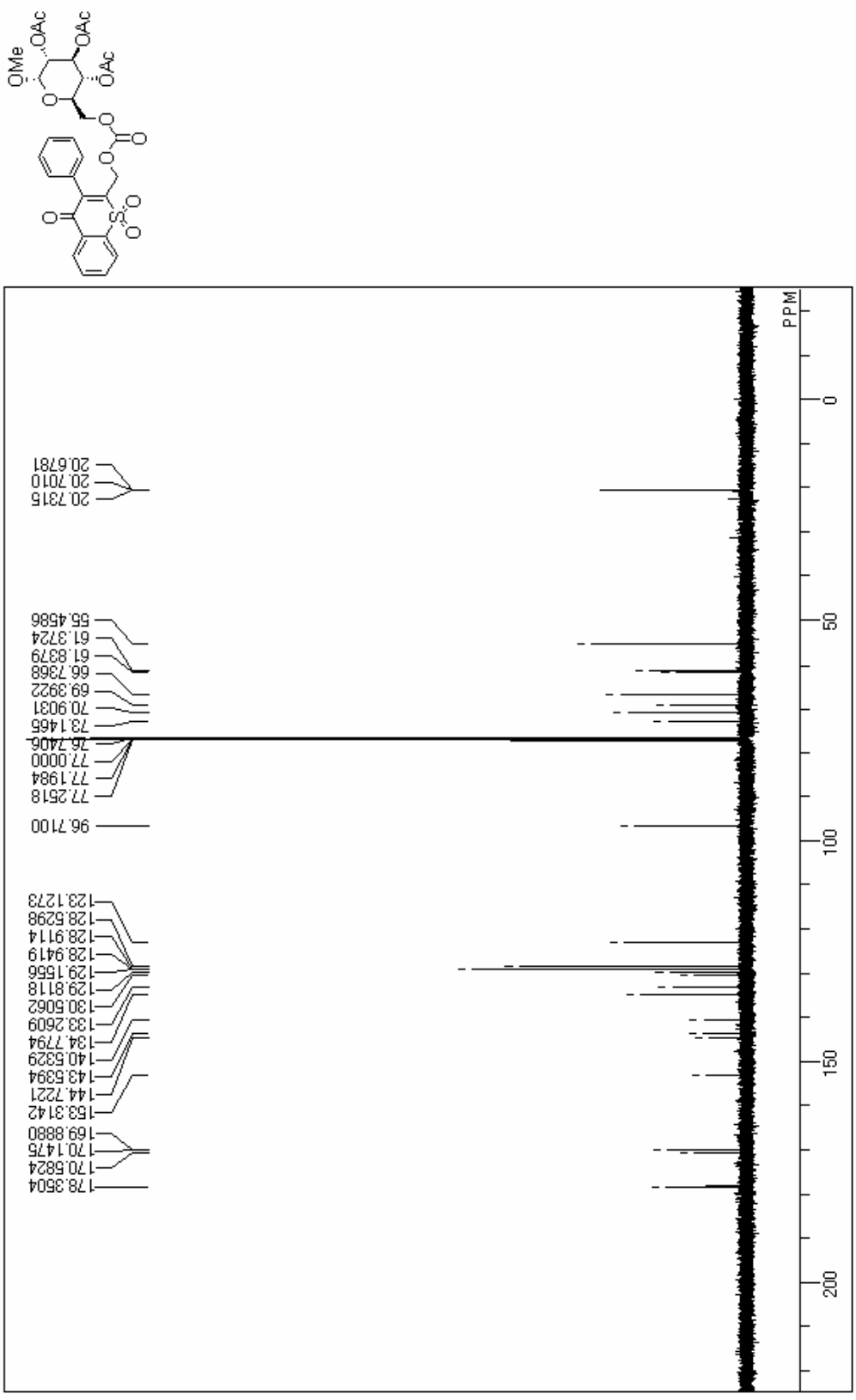
220.6624

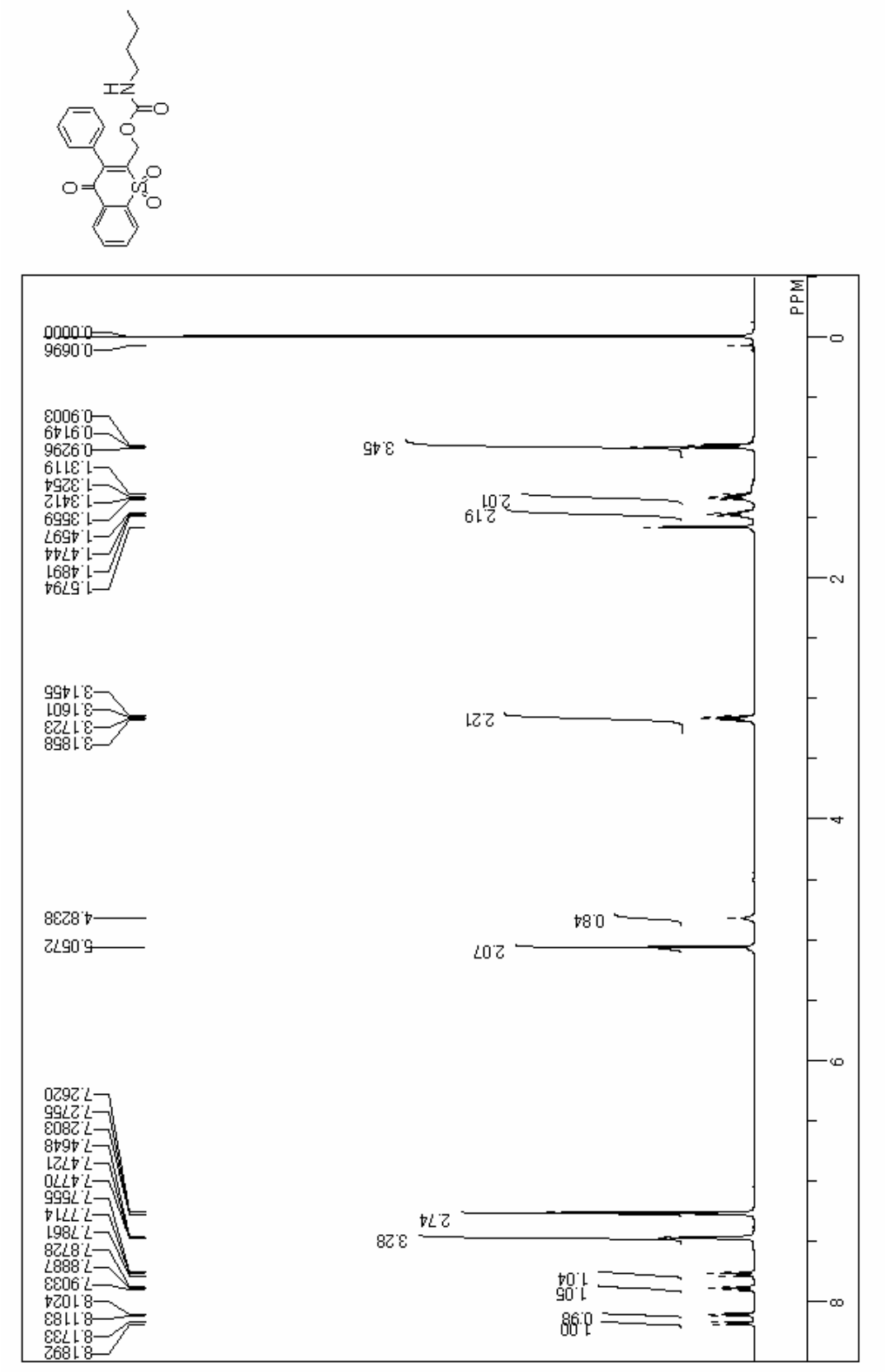
**9h**



**9h**



**9i**


PPM
0
2
4
6
8
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1.3412
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1.5794
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3.1601
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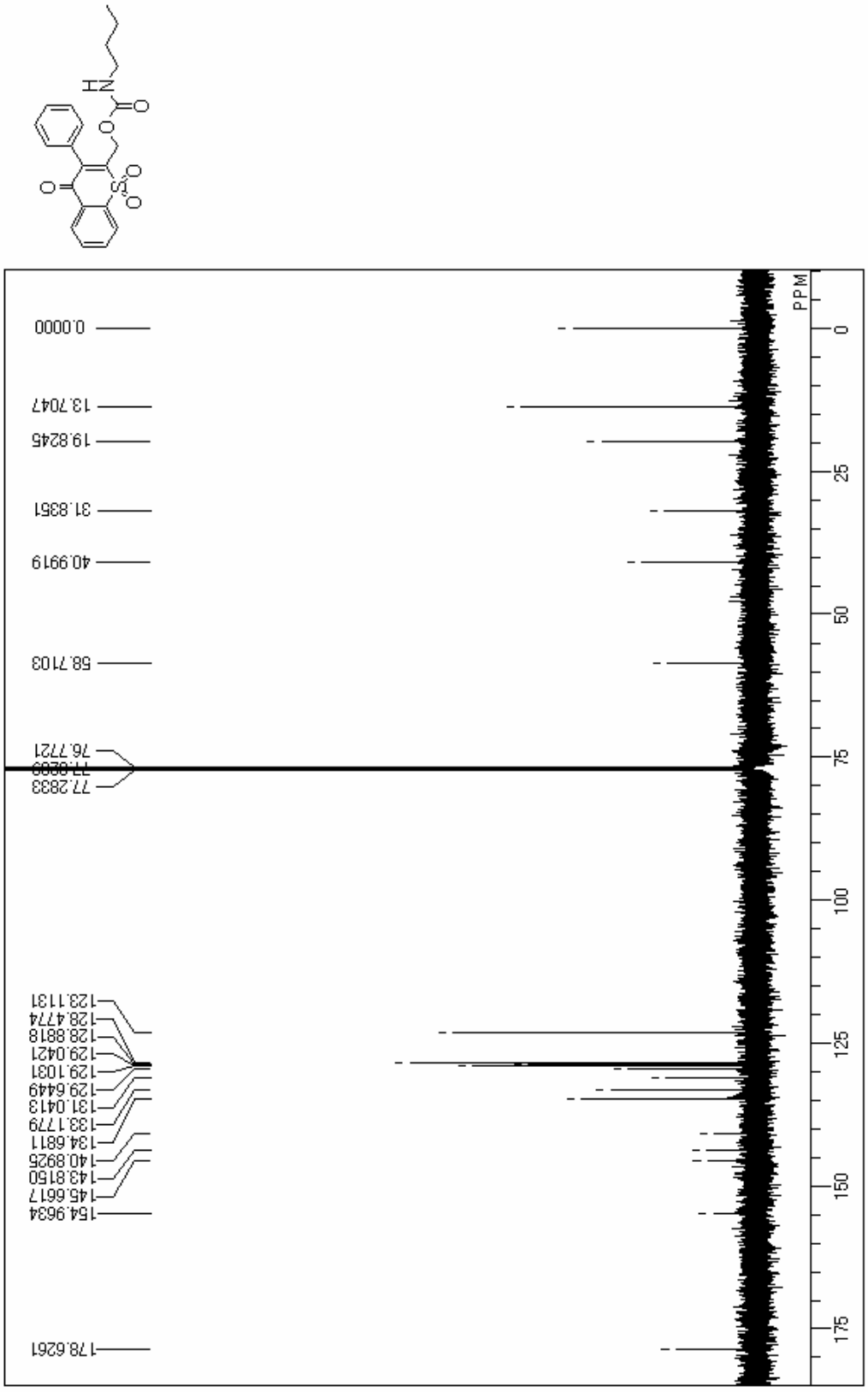
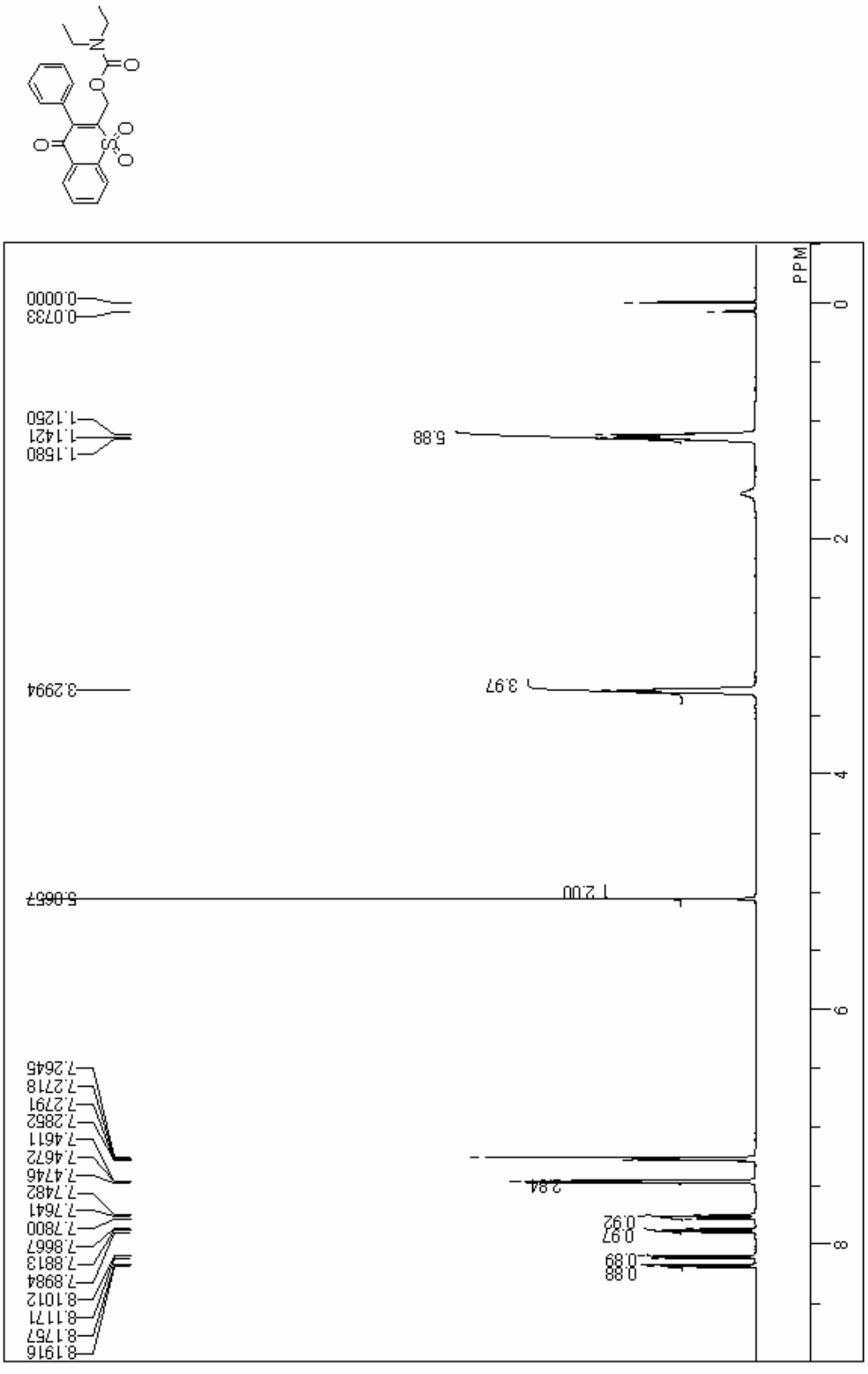
3.1858
4.8238
5.0572
7.2620
7.2755
7.2803
7.4648
7.4721
7.4770
7.7555
7.7714
7.7861
7.8728
7.8887
7.9033
8.1024
8.1183
8.1733
8.1892
3.45
2.01
2.19
2.21
0.84
2.07
2.74
3.28
1.04
1.05
0.98
1.00

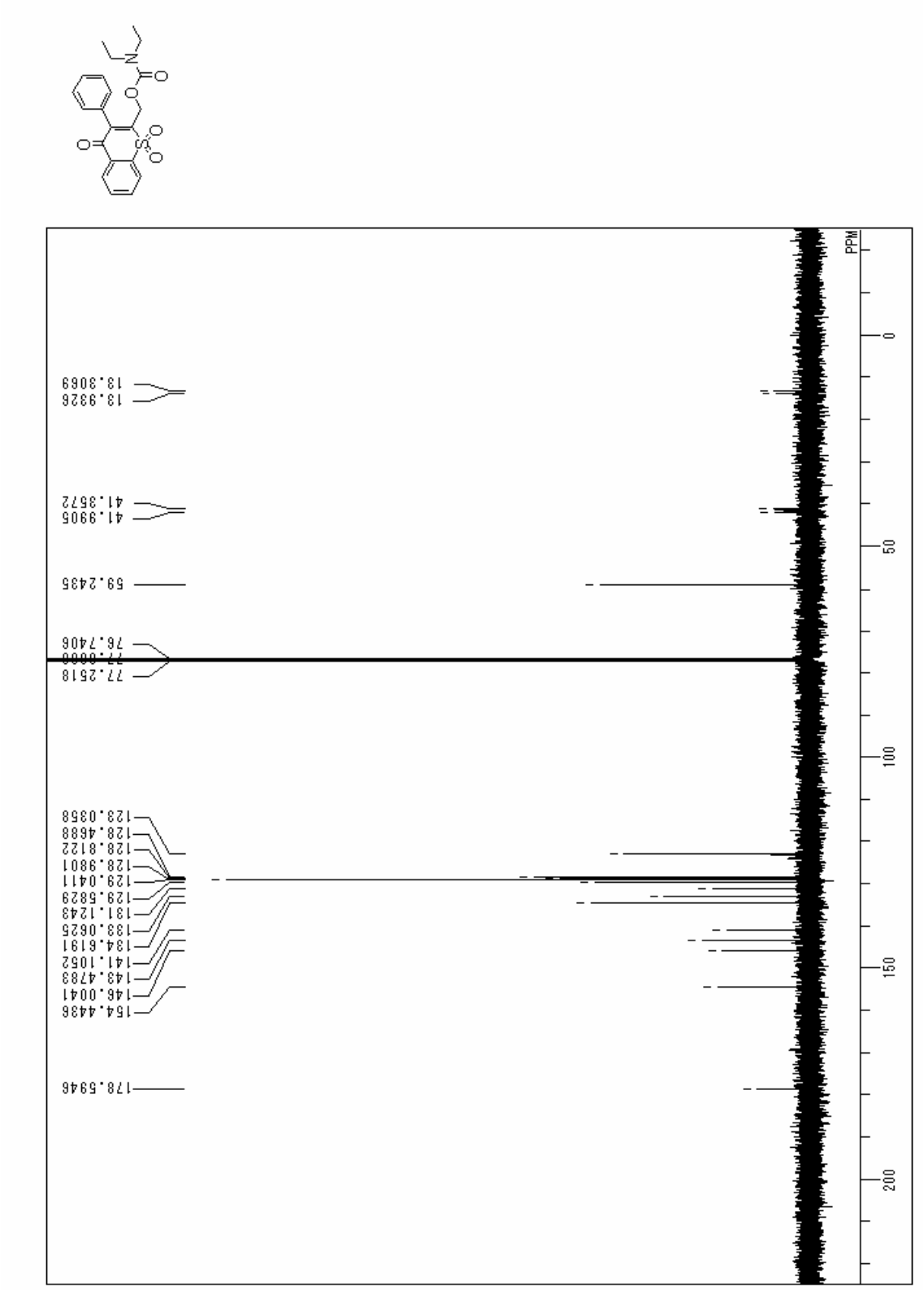
**9i**


0.0000
13.7047
19.8245
31.8351
40.9919
58.7103
76.7721
77.0889
77.2833
123.1131
128.4774
128.8818
129.0421
129.1031
129.6449
131.0413
133.1779
134.6811
140.8925
143.8150
145.6617
154.9634
178.6261
PPM
0
25
50
75
100
125
150
175

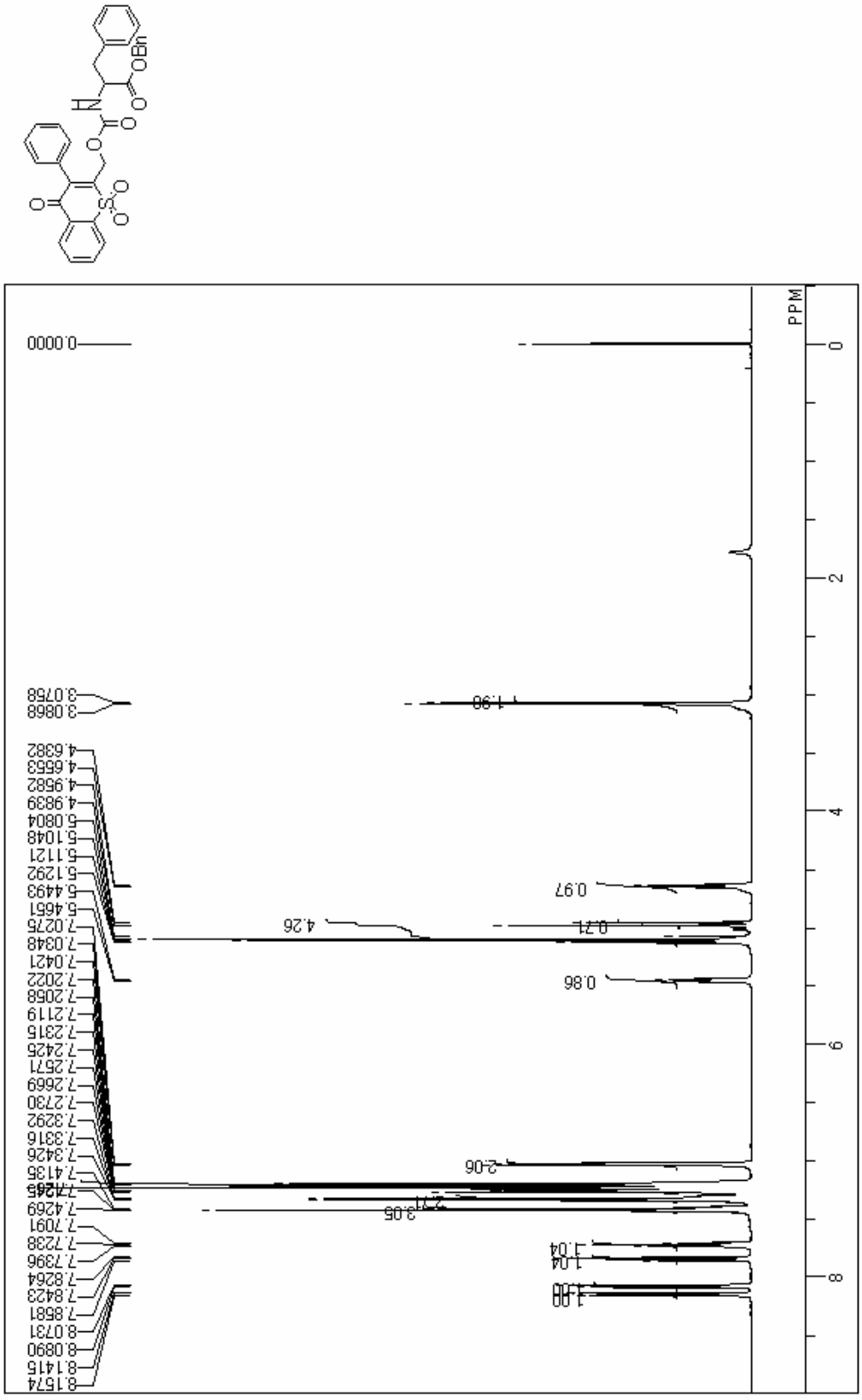
**9j**



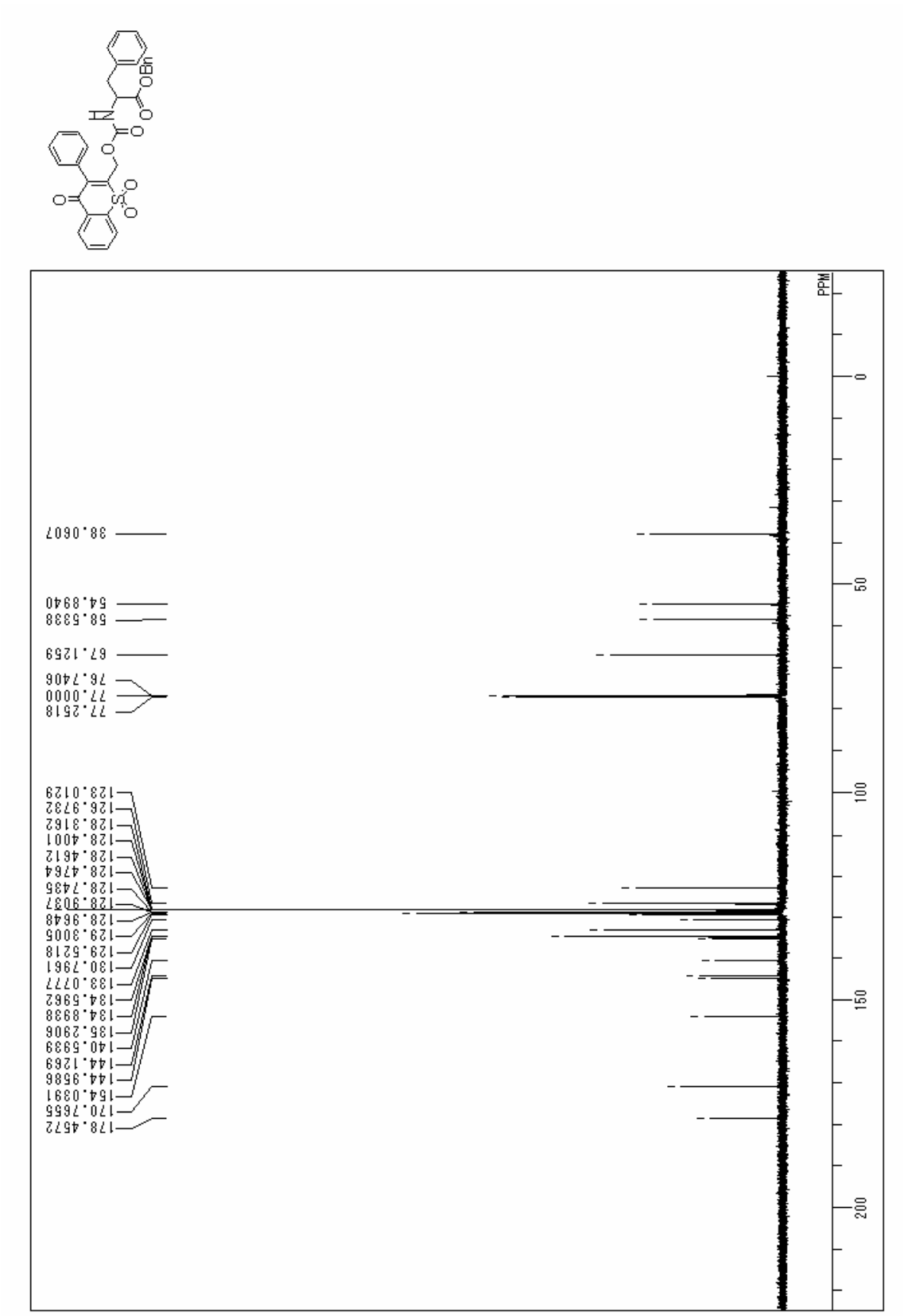
**9j**


18.3069
18.9826
41.3572
41.9905
59.2435
76.7406
77.0000
77.2518
128.0358
128.4688
128.8122
128.9801
129.0411
129.5829
131.1248
138.0625
184.6191
141.1052
148.4789
146.0041
154.4436
178.5946
PPM
0
50
100
150
200

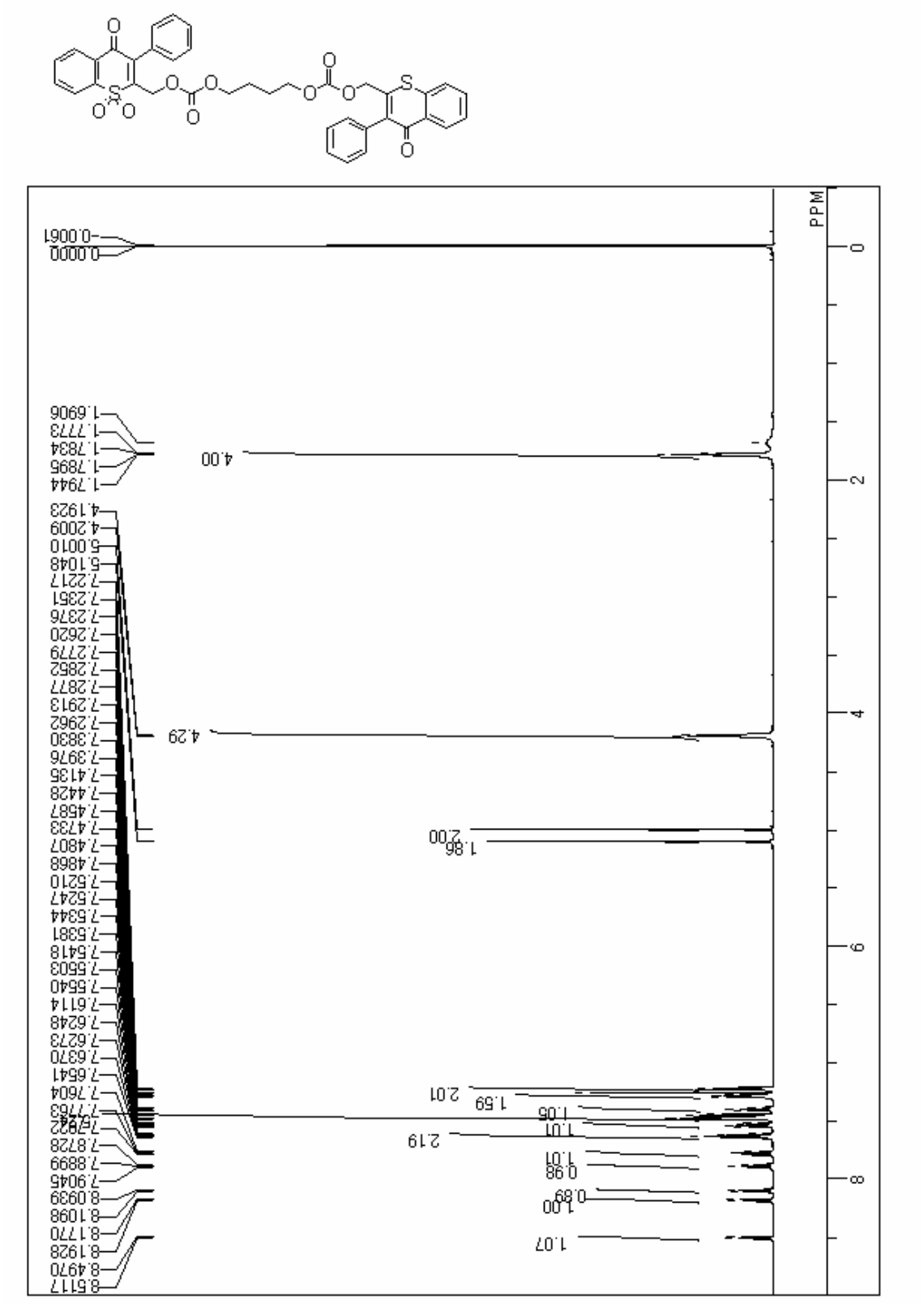
**9k**



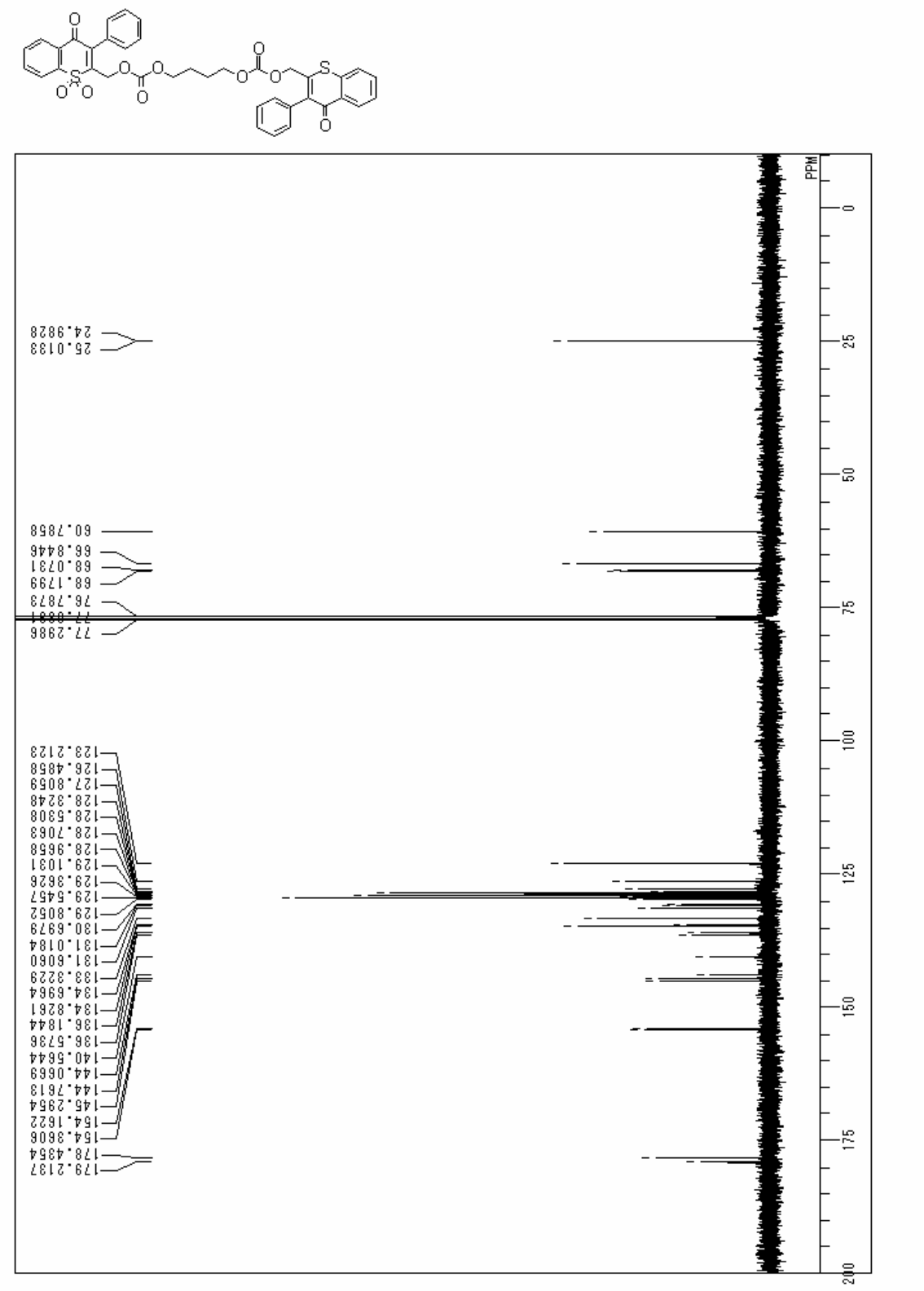
**9k**


OBn
38.0607
54.8940
58.5338
67.1259
76.7406
77.0000
77.2618
128.0129
126.9732
128.8162
128.4001
128.4612
128.4764
128.7435
128.9037
128.8648
129.3005
129.5218
130.7961
133.0777
134.5962
134.8938
135.2906
140.5939
144.1269
144.9586
154.0991
170.7655
178.4572
PPM
0
50
100
150
200

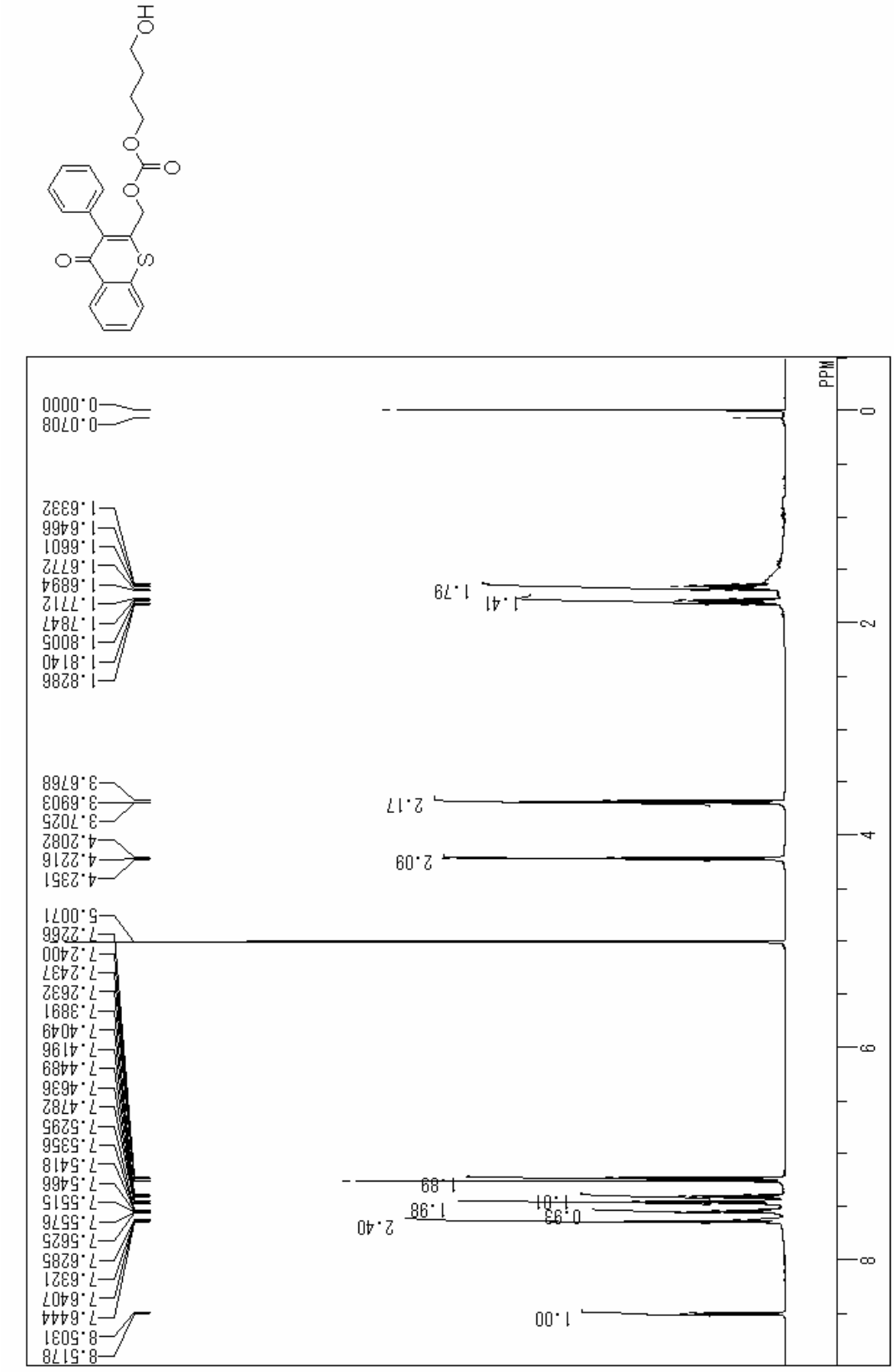
**11**



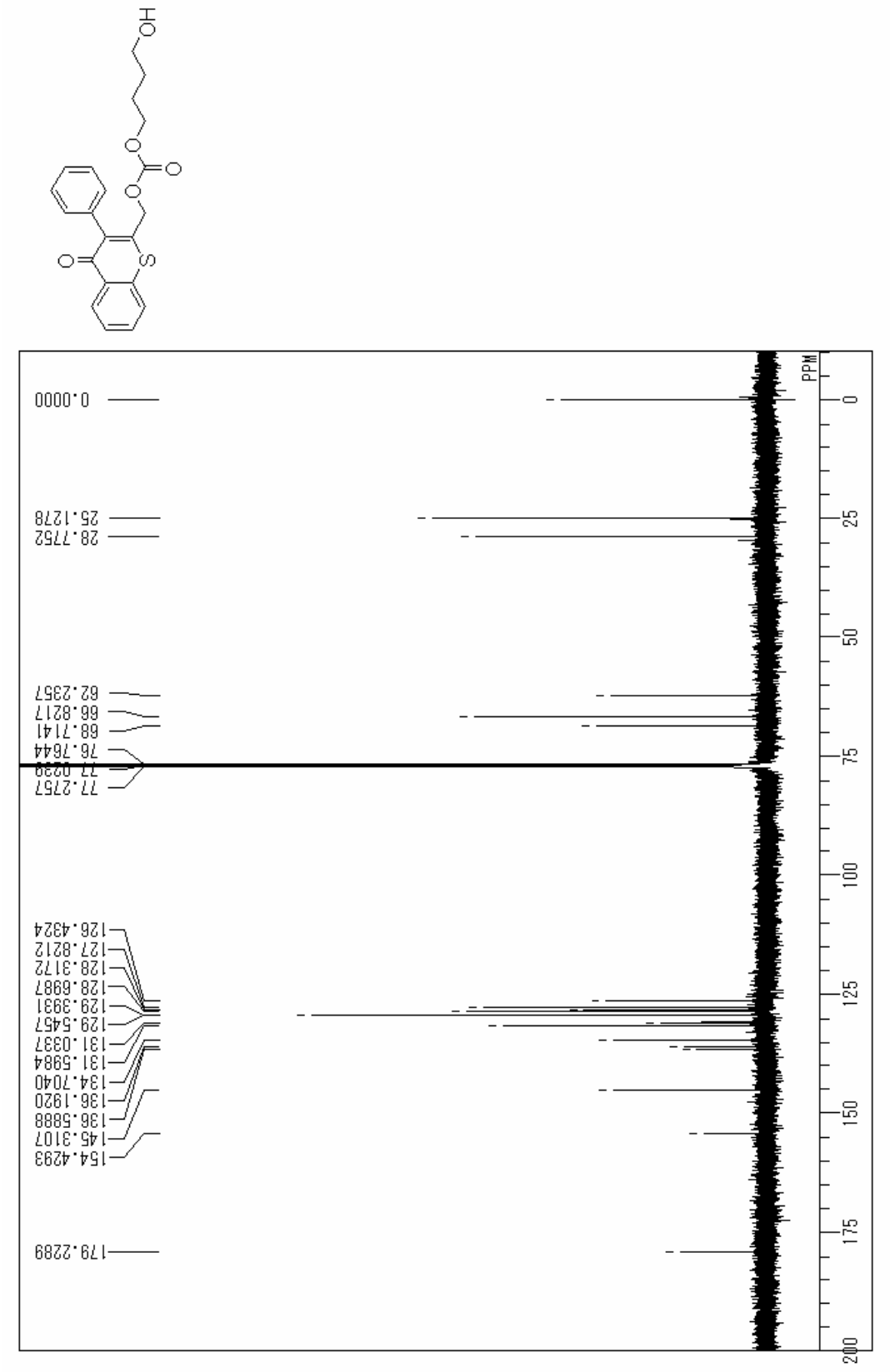
**11**


24.9828
25.0133
60.7858
66.8446
68.0731
68.1799
76.7873
77.2986
128.2128
126.4858
127.8059
128.3248
128.5308
128.7063
128.9658
129.1031
129.3826
129.5457
129.8062
130.6979
131.0184
131.6060
133.3229
134.6964
134.8261
136.1844
136.5736
140.5644
144.0669
144.7613
145.2954
154.1822
154.3606
178.4854
179.2137
PPM
0
25
50
75
100
125
150
175
200

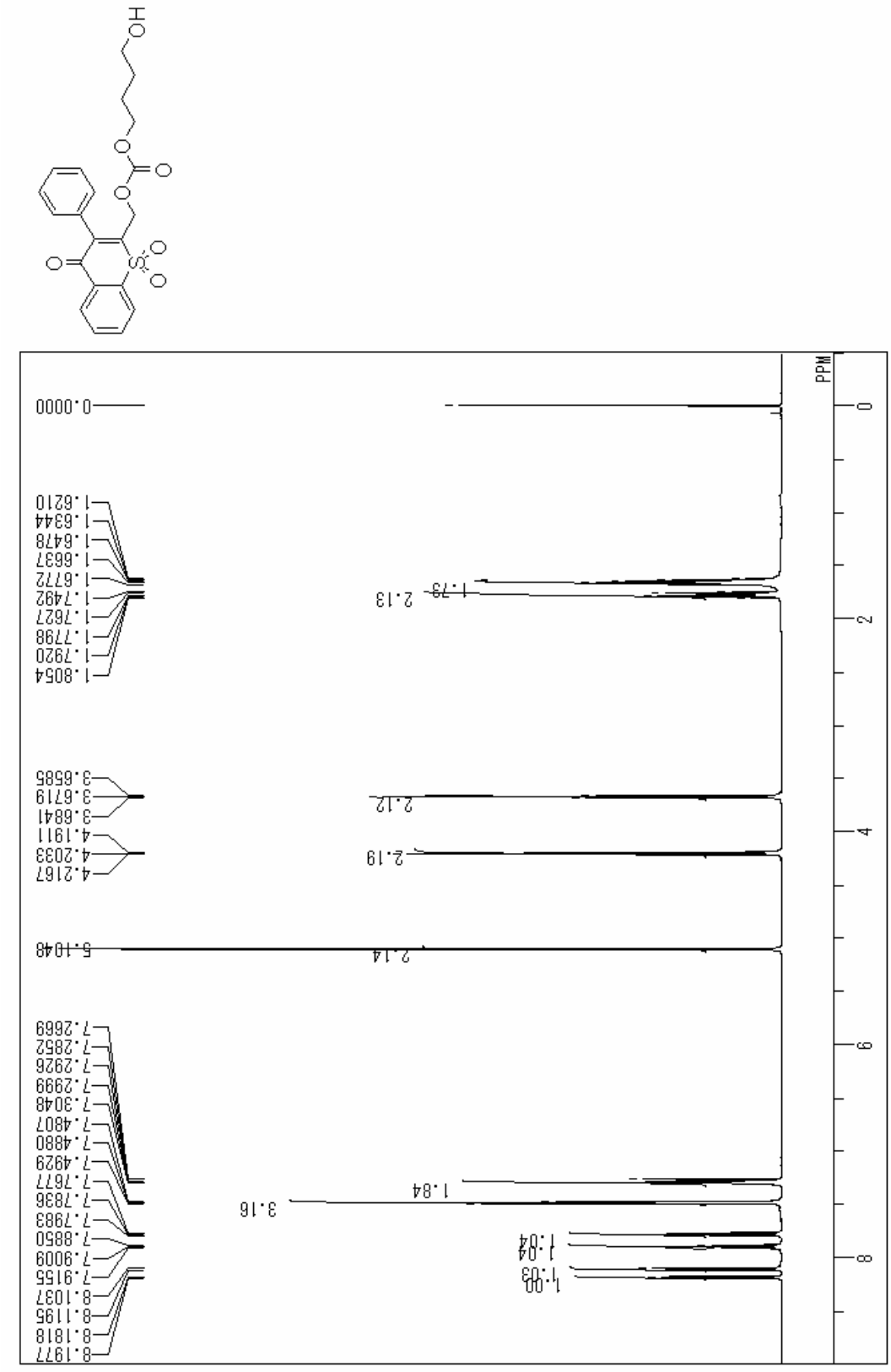
**12**


OH
O
O
O
O
S
PPM
0
2
4
6
8
0.0000
0.0708
1.6332
1.6466
1.6601
1.6772
1.6894
1.7712
1.7847
1.8005
1.8140
1.8286
3.6768
3.6903
3.7025
4.2082
4.2216
4.2351
5.0071
7.2266
7.2400
7.2437
7.2632
7.3891
7.4049
7.4196
7.4489
7.4636
7.4782
7.5295
7.5356
7.5418
7.5466
7.5515
7.5576
7.5625
7.6285
7.6321
7.6407
7.6444
8.5031
8.5178
1.79
1.41
2.17
2.09
1.89
1.98
1.01
0.99
2.40
1.00

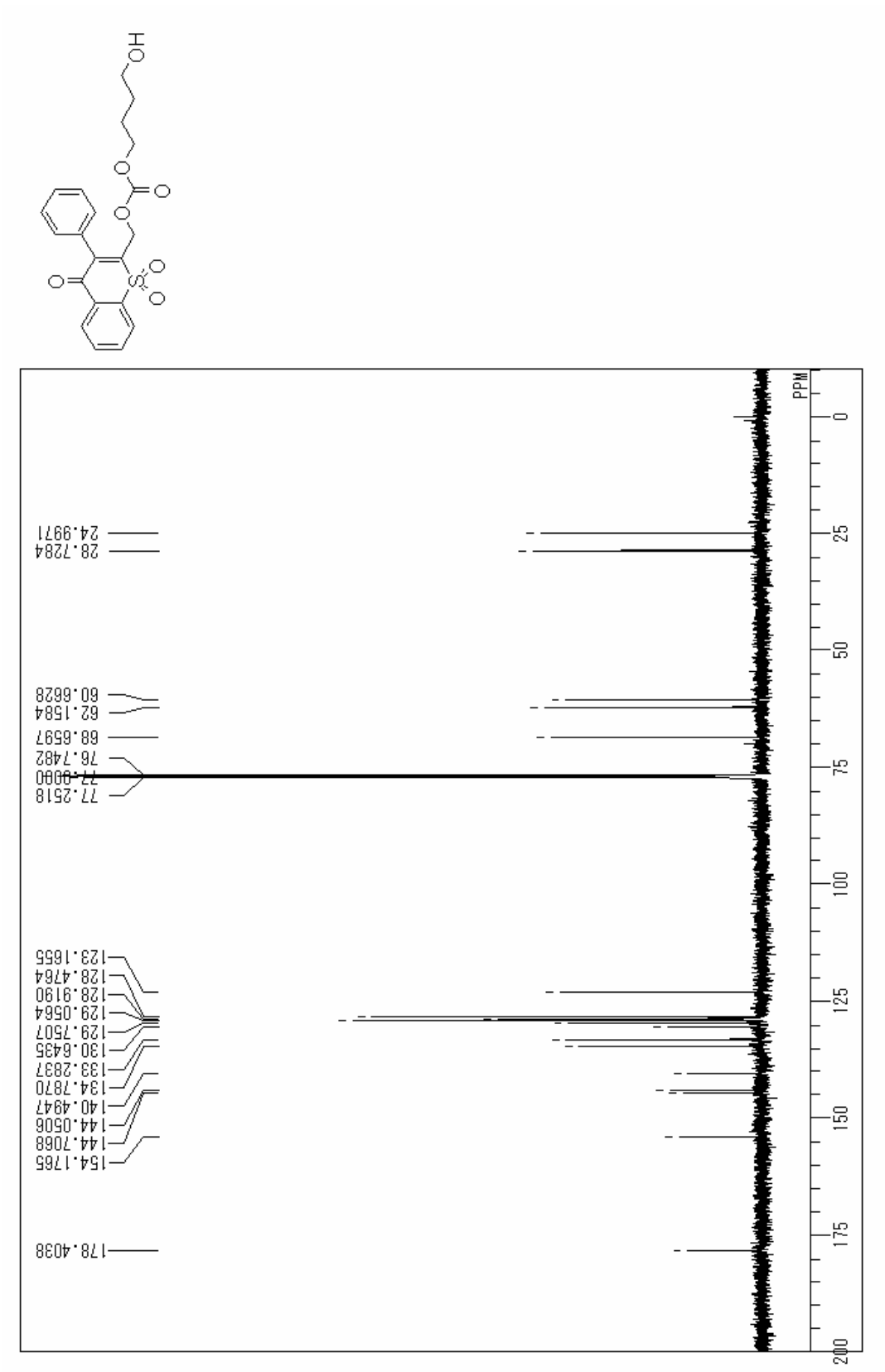
**12**


OH
O
O
O
O
O
S
0.0000
25.1278
28.7752
62.2357
66.8217
68.7141
76.7644
77.0239
77.2757
126.4324
127.8212
128.3172
128.6987
129.3931
129.5457
131.0337
131.5984
134.7040
136.1920
136.5888
145.3107
154.4293
179.2289
PPM
0
25
50
75
100
125
150
175
200

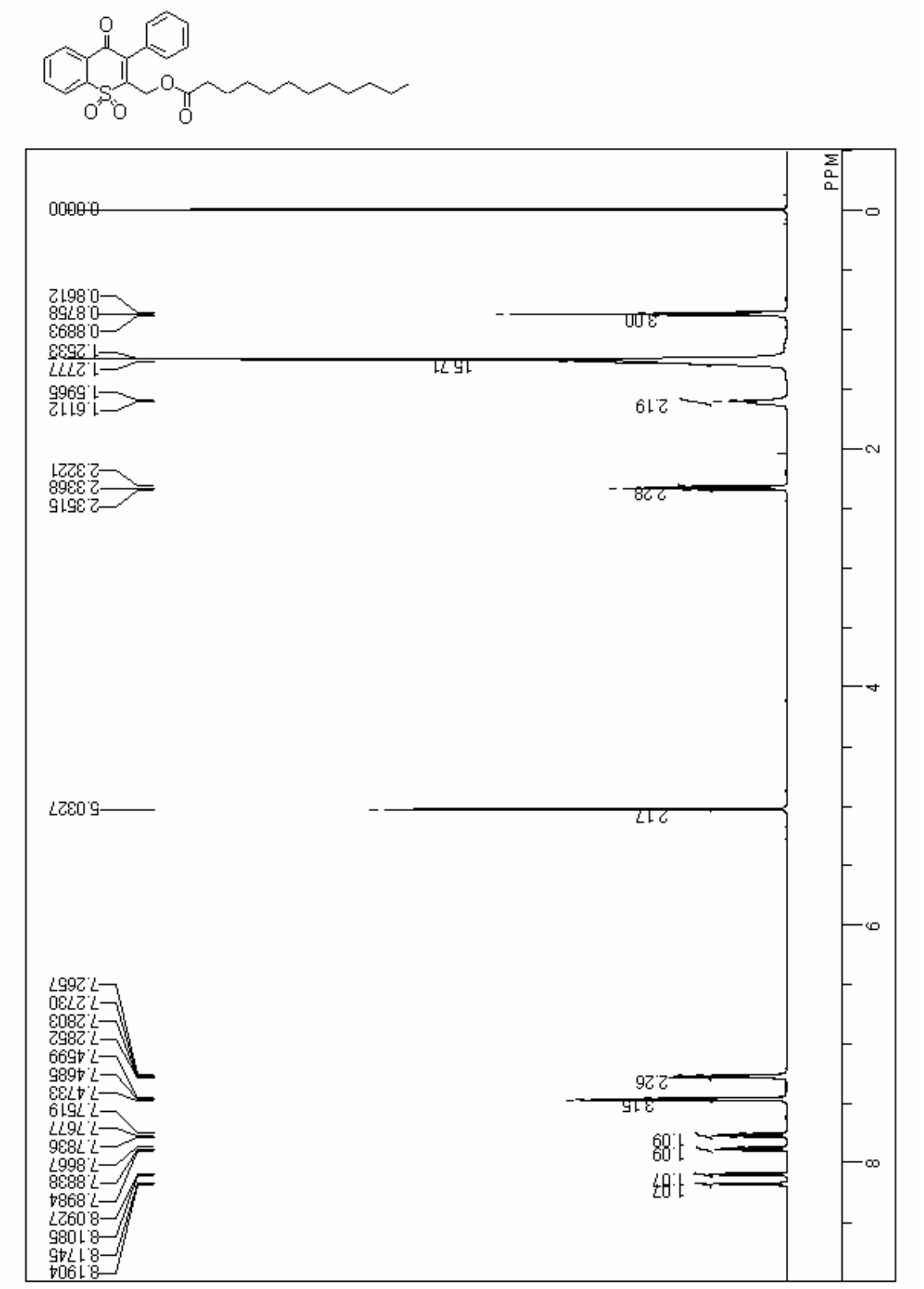
**13**


OH
O
O
O
O
O
S
O
O
PPM
0
2
4
6
8
0.0000
1.6210
1.6344
1.6478
1.6637
1.6772
1.7492
1.7627
1.7798
1.7920
1.8054
1.79
2.13
3.6585
3.6719
3.6841
4.1911
4.2033
4.2167
2.12
2.19
5.1048
2.14
7.2669
7.2852
7.2926
7.2999
7.3048
7.4807
7.4880
7.4929
7.7677
7.7836
7.7983
7.8850
7.9009
7.9155
8.1037
8.1195
8.1818
8.1977
1.84
3.16
1.00
1.84

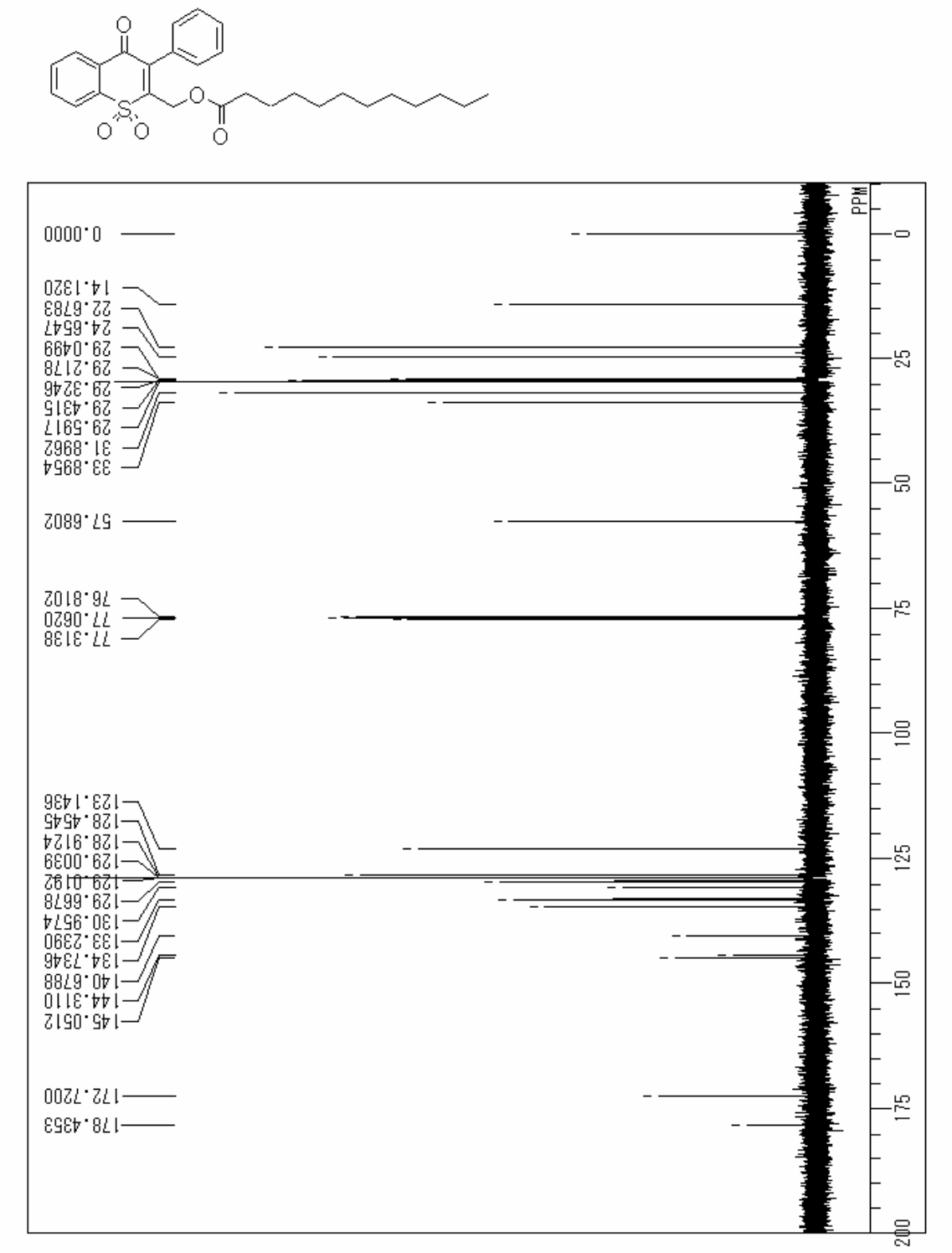
**13**


OH
O
O
O
O
O
S
O
O
24.9971
28.7284
60.6628
62.1584
68.6597
76.7482
77.0000
77.2618
123.1655
128.4764
128.9190
129.0564
129.7507
130.6435
133.2837
134.7870
140.4947
144.0506
144.7068
154.1765
178.4038
PPM
0
25
50
75
100
125
150
175
200

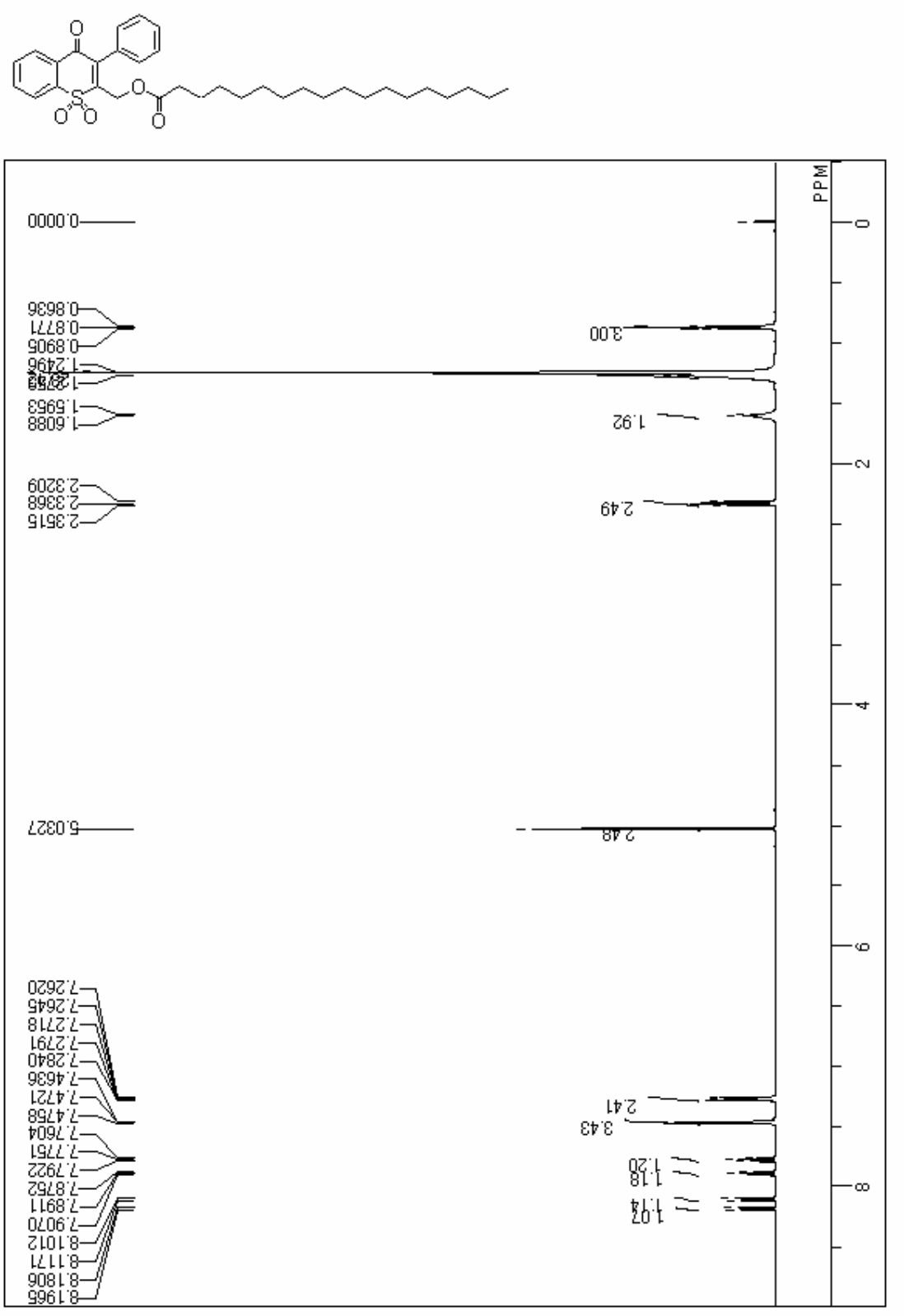
**14a**


PPM
0
2
4
6
8
0.0000
0.8612
0.8758
0.8893
1.2533
1.2777
1.5965
1.6112
2.3221
2.3368
2.3515
5.0327
7.2657
7.2730
7.2803
7.2852
7.4599
7.4685
7.4733
7.7519
7.7677
7.7836
7.8667
7.8838
7.8984
8.0927
8.1085
8.1745
8.1904
3.00
15.71
2.19
2.28
2.17
2.26
3.15
1.09
1.07

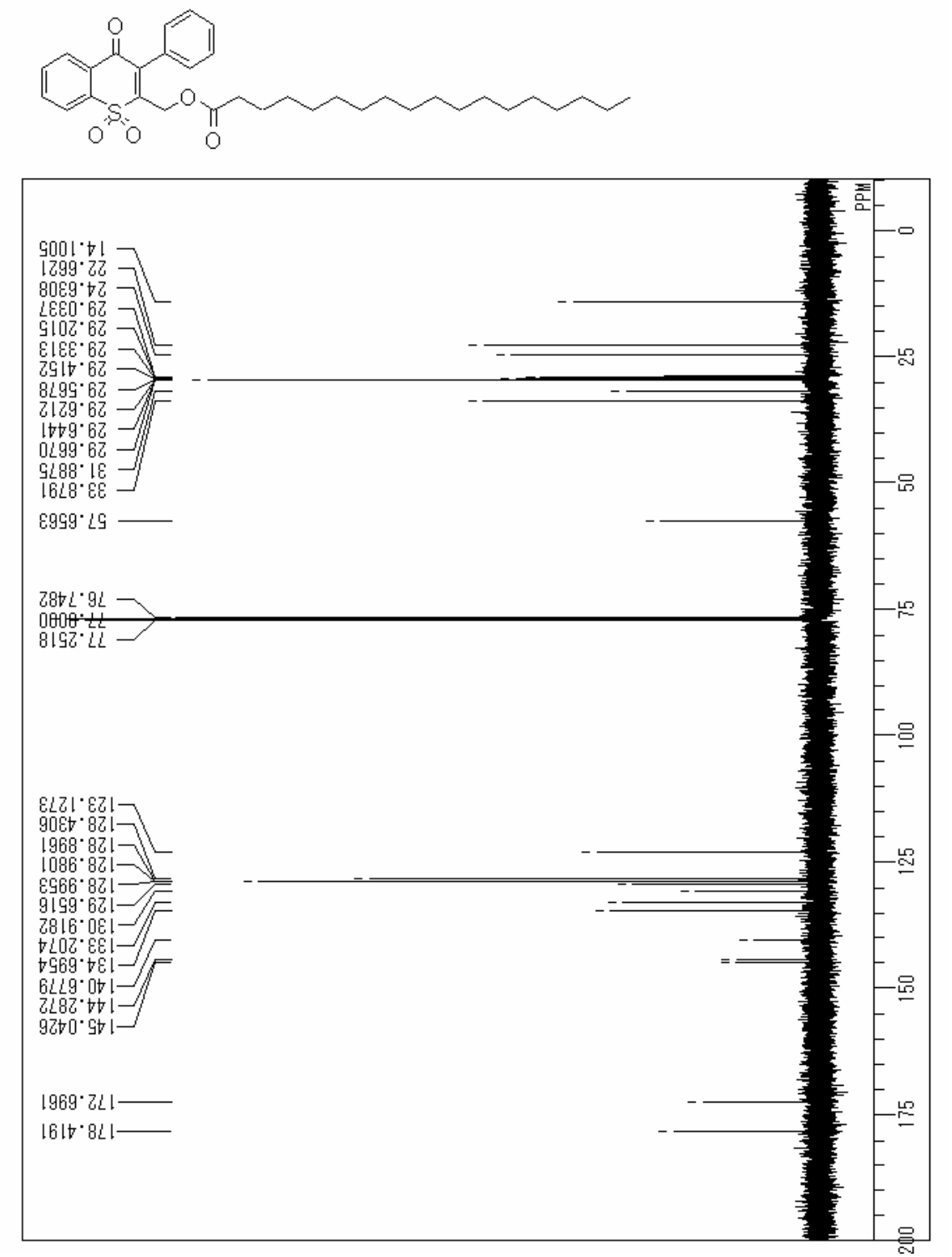
**14a**


0.0000
14.1320
22.6783
24.6547
29.0499
29.2178
29.3246
29.4315
29.5917
31.8962
33.8954
57.6802
76.8102
77.0620
77.3138
123.1436
128.4545
128.9124
129.0039
129.0192
129.6678
130.9574
133.2390
134.7346
140.6788
144.3110
145.0512
172.7200
178.4353
PPM
0
25
50
75
100
125
150
175
200

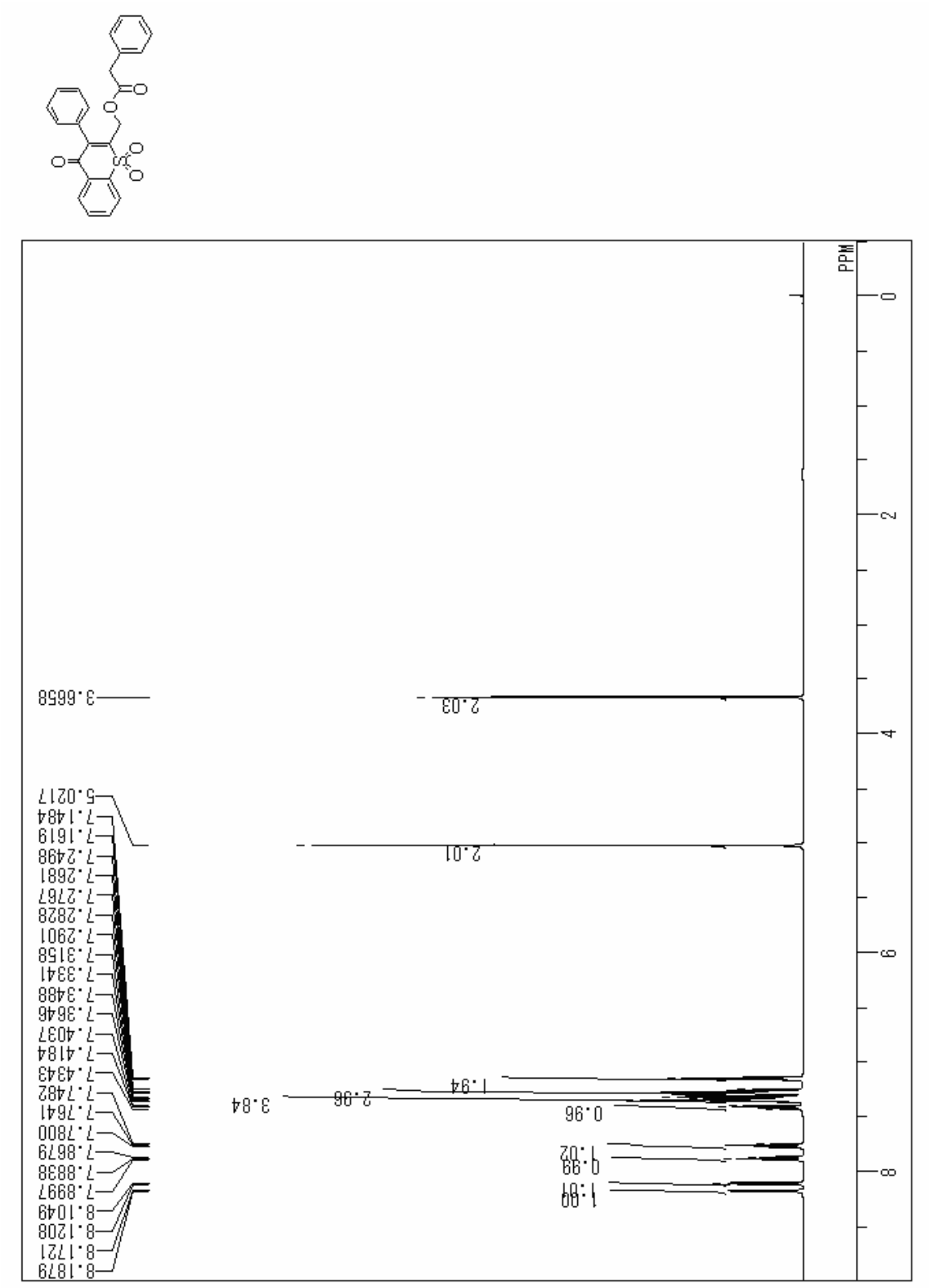
**14b**



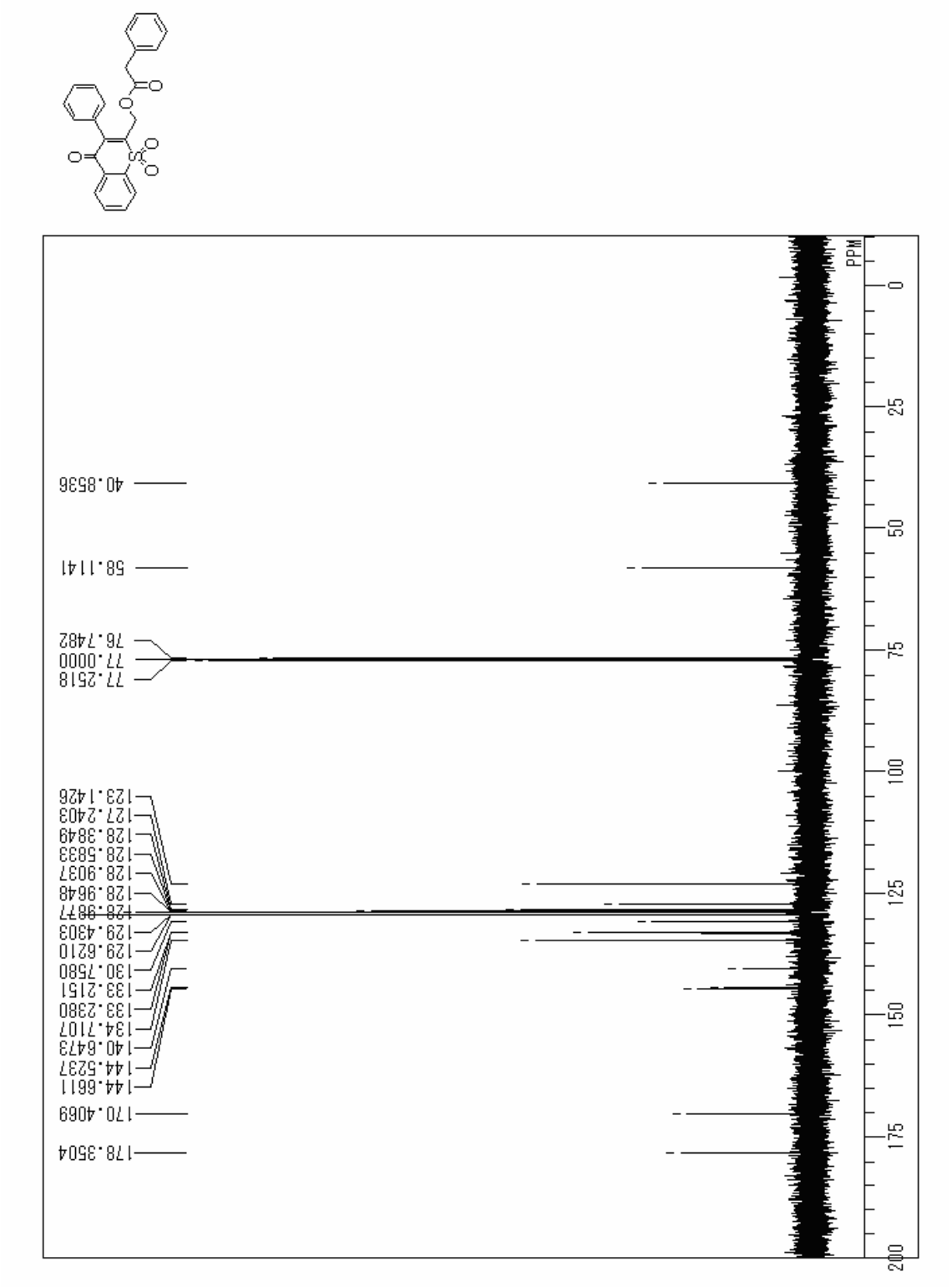
**14b**


14.1005
22.6621
24.6308
29.0337
29.2015
29.3313
29.4152
29.5678
29.6212
29.6441
29.6670
31.8875
33.8791
57.6563
76.7482
77.2518
123.1273
128.4306
128.8961
128.9801
128.9953
129.6516
130.9182
133.2074
134.6954
140.6779
144.2872
145.0426
172.6961
178.4191
PPM
0
25
50
75
100
125
150
175
200

**14c**


PPM
0
2
4
6
8
3.6658
2.03
2.01
1.94
2.06
3.84
0.96
1.02
0.99
1.01
5.0217
7.1484
7.1619
7.2498
7.2681
7.2767
7.2828
7.2901
7.3158
7.3341
7.3488
7.3646
7.4037
7.4184
7.4343
7.7482
7.7641
7.7800
7.8679
7.8838
7.8997
8.1049
8.1208
8.1721
8.1879

**14c**


40.8536
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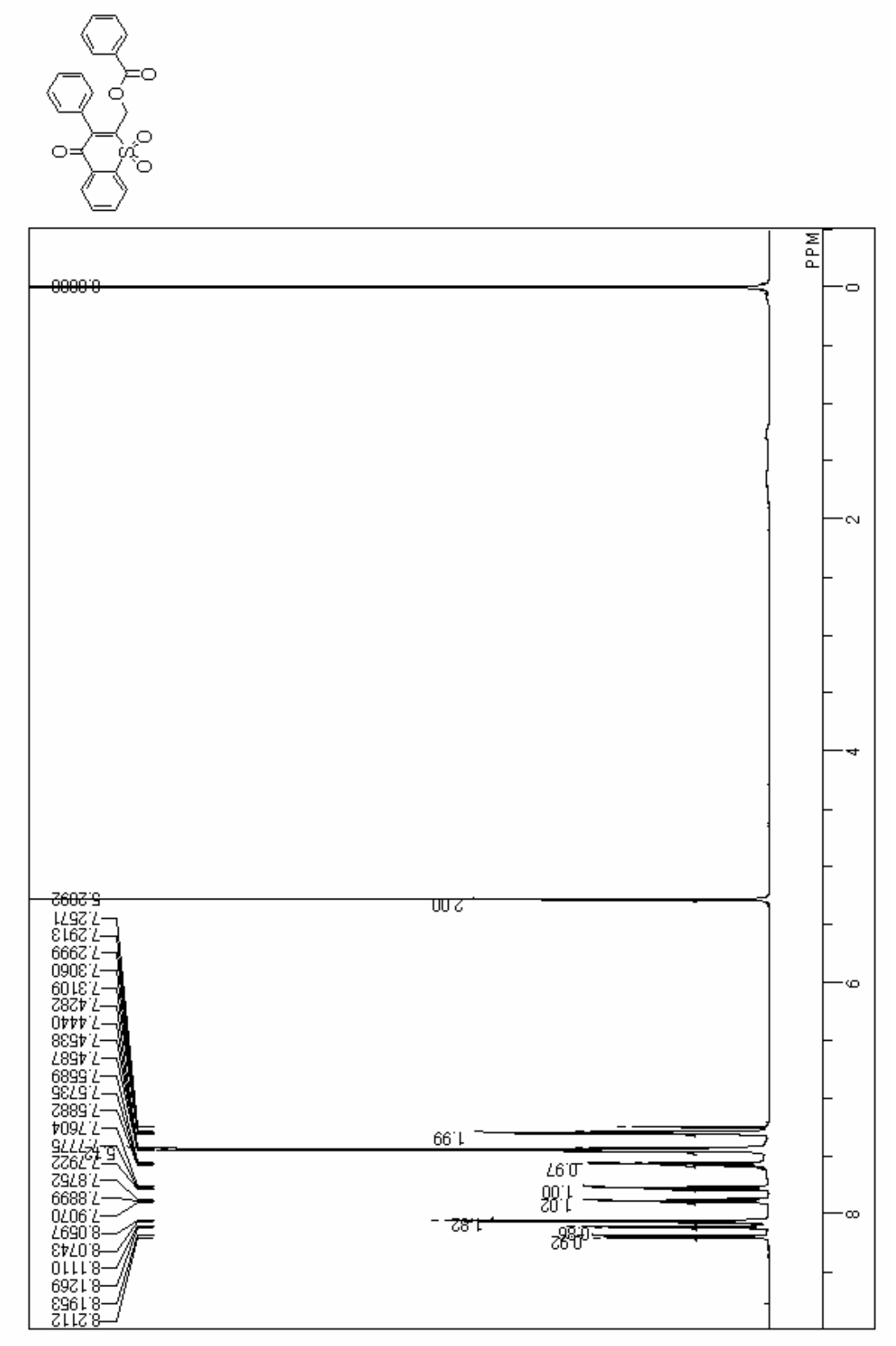
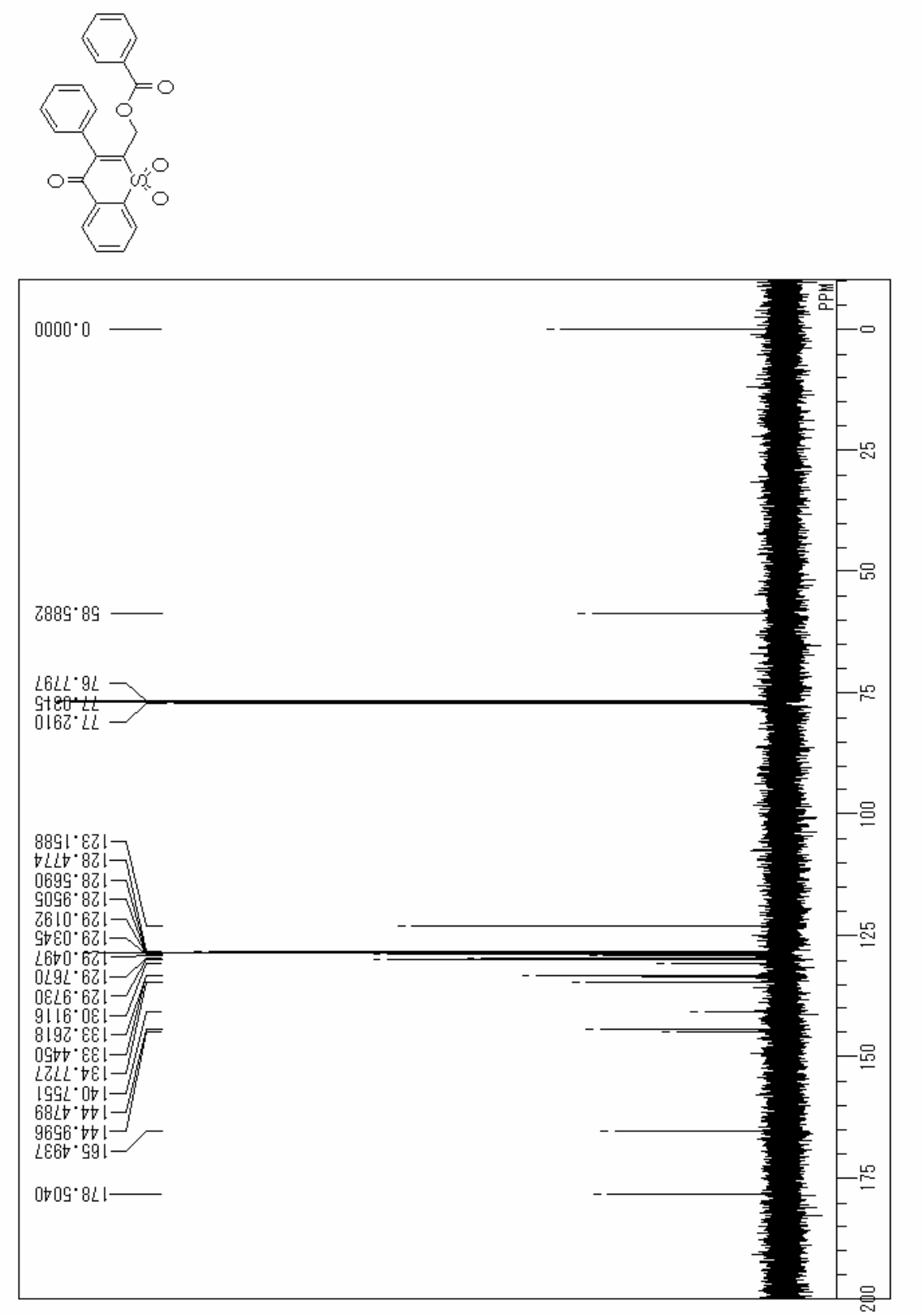
76.7482
77.0000
77.2618
123.1426
127.2403
128.3849
128.5833
128.9037
128.9648
129.4303
129.6210
130.7580
133.2151
133.2380
134.7107
140.6473
144.5237
144.6611
170.4069
178.3504
PPM
0
25
50
75
100
125
150
175
200

**14d**



**14d**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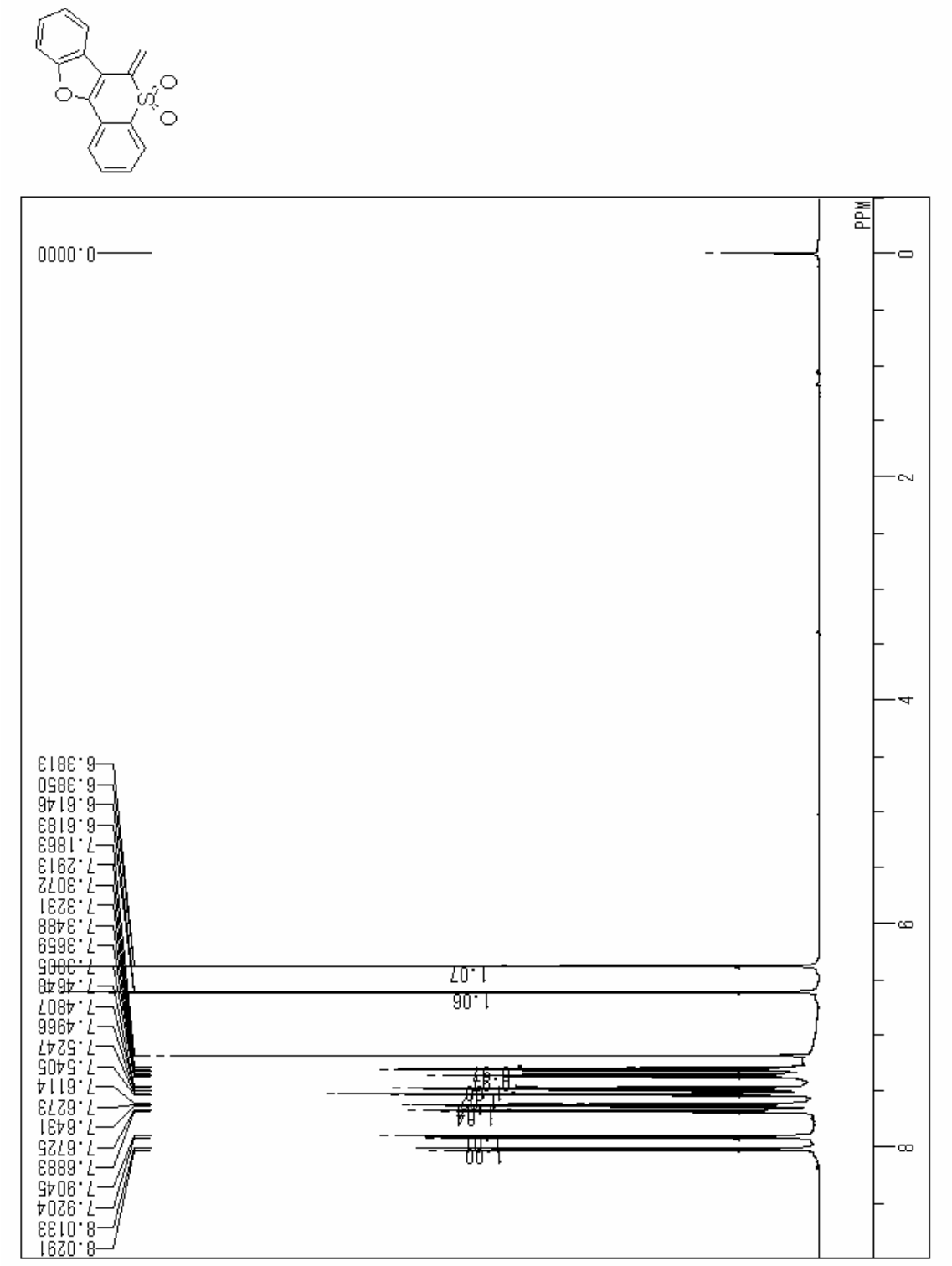
58.5882
76.7797
77.0815
77.2910
123.1588
128.4774
128.5690
128.9505
129.0192
129.0345
129.0497
129.7670
129.9730
130.9116
133.2618
133.4450
134.7727
140.7551
144.4789
144.9596
165.4937
178.5040
PPM
0
25
50
75
100
125
150
175
200

**10**


PPM
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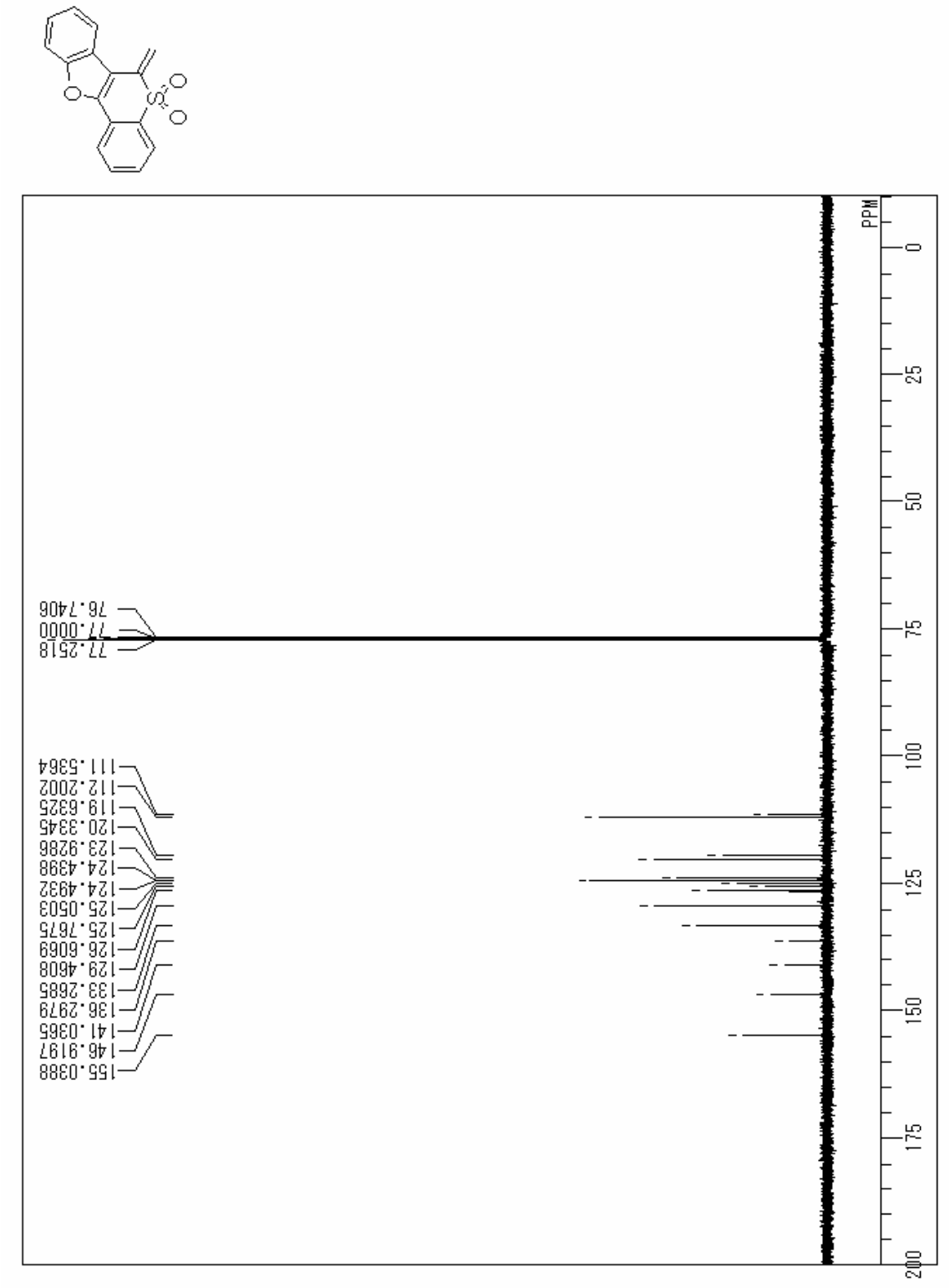
2
4
6
8
0.0000
6.3813
6.3850
6.6146
6.6183
7.1863
7.2913
7.3072
7.3231
7.3488
7.3659
7.3805
7.4648
7.4807
7.4966
7.5247
7.5405
7.6114
7.6273
7.6431
7.6725
7.6883
7.9045
7.9204
8.0133
8.0291
1.07
1.06

**10**


PPM
0
25
50
75
100
125
150
175
200
77.2518
77.0000
76.7406
111.5364
112.2002
119.6325
120.3345
123.9286
124.4398
124.4932
125.0503
125.7675
126.6069
129.4608
133.2685
136.2979
141.0365
146.9197
155.0388